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THE ABSORPTION SPECTRA OF VARIOUS SALTS IN SOLUTION AND THE EFFECT OF TEMPERATURE ON SUCH SPECTRA.[1]

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(A report on part of the work on absorption spectra that is being carried out with the aid of a Grant from the Carnegie Institution of Washington.)

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[1] Part I of this paper was published in THIS JOURNAL, **43**, 37.

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The study of the various phenomena of light may be divided into three parts: The emission of light by matter, the transmission of light through space and the absorption of light by matter. The theory of the transmission of light as an electromagnetic phenomenon was first proposed by Faraday and Maxwell. On this theory it is assumed that in all regions of space through which light passes there are electric and magnetic fields. In an electric field there exists a certain state of things that gives rise to a force acting on any electric charge that may exist there. This is the electric force and this represents the state of the region of space considered. In a similar way the magnetic field is also defined. A relation is then found between the electromagnetic quantities which is usually called Maxwell's equations, or is a modified form of these equations. Starting with these equations Maxwell showed that the state of things represented by his fundamental equations consists of the propagation of a periodic variation of the electric and magnetic forces through space with the velocity of light. So well do the nature of these electromagnetic waves agree with the properties of light as transmitted by the ether and transparent bodies that light is at present considered to be an electromagnetic disturbance itself. The simplest case of light waves is that of plane polarized waves traveling in the direction of the x axis. Waves of this kind are:

$$E_y = a \cos n\left(t - \frac{x}{c}\right), \quad H_z = a \cos n\left(t - \frac{x}{c}\right).$$

E_y, the component of the electric force in the y direction, is the only component of the electric force that has a value. The magnetic force has a component only in the z direction, H_z. a is the amplitude of the disturbance, t is the time, n is the number of vibrations in a time 2π and c is the velocity of light.

I. Recent Spectroscopic Investigations.

A light wave in the "ether" is an electromagnetic disturbance that is propagated in free space without any distortion of form or any dissipation of energy, one of the properties of electric and magnetic fields being the power to store energy. When a light wave strikes ordinary matter it is in general broken up into several parts. If the surface of the body is smooth, a considerable part of the energy will be taken up by a regularly reflected wave. If the surface is rough, a great number of so-called waves will be reflected. The remaining part of the disturbance will advance through the body. As no body is a perfect reflector or absolutely transparent, it follows that part of the energy of the light wave remains with the body. This phenomenon is known as the absorption of light. We also know of many conditions of matter in which light is emitted. The object of the study of emission and absorption of light is to gain some knowledge of the mechanism of matter by which it is enabled to produce or absorb electromagnetic waves. The expression of the properties of different kinds of matter by different values of the dielectric constant (κ), the conductivity (σ) or the magnetic permeability (μ) has not been found to be satisfactory.

The electromagnetic mechanism which at present is considered as the basis of the theories of radiation and absorption is the electron. The charge which it carries has been found to be the atomic unit of electricity. Experimental results in electricity can be explained on this basis. The electron is found in the vacuum discharge tube, in the radiations from radioactive matter, in arcs, in sparks, in secondary radiations. They are present in all bodies. By the distribution and motions of these electrons scientists of to-day at-

tempt to explain all electrical and optical phenomena. Some electrons in a conducting body are in a free state so that they can obey an electric force. Richardson and Brown[1] have shown that ions emitted by hot platinum (and approximately so for other metals) are kinetically identical with the molecules of a gas, of equal molecular weight, at the temperature of the metal. This holds for the mode of distribution of velocity as well as its average value. This shows that the free electrons inside the metal have the same amount and mode of distribution of velocity and kinetic energy as the molecules of a gas of equal molecular weight at the temperature of the metal.

In the case of a nonconducting substance the electrons are considered as bound to certain positions of equilibrium. In a conductor in an electric field there is an excess of electrons at one end. In a dielectric, as soon as an electron is displaced from a position of equilibrium, a new (elastic) force is brought into play which pulls the electron back to its original position. The motion of electrons in nonconducting bodies, together with the change of dielectric displacement of the ether itself, makes up Maxwell's displacement current. Under the influence of the elastic forces the electrons can vibrate about their positions of equilibrium and may thus become the centers of electromagnetic waves. In this way may be explained the emission of light and heat. Absorption results when the electrons are set into vibration by a beam of light and part of the vibrating energy of the electron is transformed into heat energy.

As to the nature of the electron very little is known. On the other hand, the mathematical electron is much better known. As the recent experiments by Bucherer[2] on the value of e/m agree with values calculated by Lorenz, use will be made here of his conception of the electron. To each electron is ascribed certain definite dimensions. The ether is assumed to pervade not only the space between atoms but also the space within atoms and electrons. This ether is assumed to

[1] Phil. Mag., Sept., 1908; Dec., 1908.
[2] Physik. Z., Nov., 1908, p. 755.

be at rest. There will be an electromagnetic field within the electron as well as without. Various distributions of charge may be assumed. Lorentz usually assumes a volume density (ρ) distribution such that ρ is a continuous function of the coördinates. The charged particle has then no sharp boundary but is surrounded by a thin layer in which the density gradually sinks from ρ to 0. The ether is simply the space in which a certain state of the electromagnetic field exists. (Recently very interesting papers by Einstein and others on this subject have appeared.) The electron having been thus defined, equations can be formed for the electric and magnetic fields for any region in which there are electrons either at rest or in motion. Having considered the elementary unit of the mechanism of optical phenomenon let us now turn to some of the phenomena themselves.

(*a*) *Spectra of Gases.*—For optical purposes bodies may be divided into gases and into solids and liquids. The spectra of gases consist of an enormous number of fine lines and are usually grouped into line and band spectra. Band spectra themselves consist of a great number of sharp lines spaced in a very regular manner, whereas line spectra consist of lines apparently spaced more or less at random in the spectrum although some of the lines have been found to have frequencies that are connected by certain series relations. Good examples of band spectra are the absorption spectra of fluorine, bromine, iodine, chlorine, sulphur or sodium vapors. These consist of thousands of very fine lines. Very interesting work has recently been done by Wood on the magnetic rotation spectrum and the fluorescent spectrum of sodium vapor. On exciting fluorescence by monochromatic light of different wave lengths it is possible to set into vibration apparently different systems in the sodium atoms or clusters containing sodium atoms, each one of these systems of vibrators emitting a different series of bands. It is found that the presence of foreign gases has a very great effect upon the absorption spectra of sodium. The presence of hydrogen prevents fluorescence. Wood[1] found that as mercury vapor is evolved in

[1] Astrophys. J., **26**, 41 (1907).

a vacuum the band λ 2536 broadens rapidly on the less refrangible side, attaining a width of three or four hundred A. U. There is a little broadening in the other direction. If hydrogen or some other inert gas is present, the band broadens symmetrically at first. Larmor[1] has suggested that this unsymmetrical widening may be due to the formation of loose molecular aggregates, which vibrate in longer periods owing to this mutual influence. Wood and Guthrie[2] find that the cadmium absorption band λ 2288 broadens symmetrically in the case of pure cadmium but very asymmetrically when mercury is present. A very promising field for research is suggested by this work, one that will probably throw much light upon the mechanism within the atoms themselves.

Quite recently Dufour[3] has succeeded in obtaining the Zeeman phenomena for many of the bands of the emission spectrum of fluorides and chlorides of calcium, strontium, barium and silicon. These give in some cases a normal and in other cases an abnormal longitudinal Zeeman (light being parallel to the magnetic field) doublet, the normal doublet usually being considered as originating from a negative charge and an abnormal doublet as due to a positive charge. The only difference in these two effects is that the light is circularly polarized in opposite directions for corresponding components of the doublet. Dufour considers that so far all spectra (emission or absorption) that show the abnormal Zeeman effect have their centers in the molecules. If one considers the explanation to be due to positive and negative electrons, then the value of e/m for these will be about the same except in the case of some of the bands of xenotine. At the University of Manchester it has been shown that the Humphrey-Mohler pressure shift is to be observed for bands that give the Zeeman effect. With the exception of the few bands described by Dufour, the wave length of bands is unalterable by physical and chemical changes.

The band spectra are very complex indeed. In Watts'

[1] Astrophys. J., **26**, 120 (1907).
[2] *Ibid.*, **28**, 211 (1909).
[3] Physik. Z., **4**, 124 (1909).

"Index to Spectra" the wave lengths of over 5000 bands are given for sulphur between λ 6400 and λ 3600, over 2700 lines for iodine between λ 6300 and λ 5100, over 2800 for bromine between λ 6200 and λ 5100, and over 2600 for aluminium oxide between λ 5200 and λ 4400. Complex as these spectra are, the so-called line spectra of the elements are even more complex. The same author gives the wave lengths of over 2300 lines for chromium, 3000 for iridium, 2300 for iron (spark), 3000 for tungsten (spark), and 5200 for uranium (spark). For most of these elements the greatest number of lines lie in the regions of shorter wave lengths, and in most cases the maximum number of lines lie between λ 4000 and λ 3000. For example, Watts gives 1100 iron lines between $\lambda\lambda$ 2000 and 3000, over 1400 lines between $\lambda\lambda$ 3000 and 4000, 1100 lines between $\lambda\lambda$ 4000 and 5000, over 600 lines between $\lambda\lambda$ 5000 and 6000, and only a little over 300 between $\lambda\lambda$ 6000 and 6750. A similar distribution holds for vanadium, osmium, etc. The work of Schumann and Lyman shows that many more lines exist in the ultraviolet down to λ 1000, but it seems quite probable that most of the spark and arc lines lie either in the visible or in the adjacent ultraviolet regions of the spectrum.

When the source of the line spectrum is subjected to physical changes the width and relative intensities of the bands change enormously. Rayleigh[1] and Michelson[2] have shown that the Döppler effect accounts for the width of the lines when the pressure is small. Michelson gives a formula for the breadth (b) of the spectrum lines,

$$b = \sqrt{\theta m}\, \lambda(a + bd\lambda),$$

where θ is the absolute temperature, m the molecular weight, a and d constants.

At present only two physical causes are known to change the frequency of vibration of the emitters or absorbers of the line spectrum. One of these is the Humphrey-Mohler effect—that an increase of pressure about the source of light causes

[1] Phil. Mag., **27**, 298 (1889).
[2] *Ibid.*, **34**, 280 (1892).

the lines to be slightly shifted towards the red. Humphreys considers this to be due to the magnetic fields of neighboring atoms. Richardson,[1] on the other hand, considers the shift as due to electrostatic action. An increase of the partial pressure of the vapor of the emitting substance only causes the lines to widen. An increase of the total pressure of the surrounding vapor causes a shift, and this Richardson considers as due to sympathetic vibrations set up in the surrounding atoms. If an atom is emitting light it must be surrounded by an alternating field of force and this will produce forced vibrations of equal period and, under certain conditions, of equal phase in the neighboring atoms. These sympathetic vibrations will then react upon the emitting atom and increase its period. After making several assumptions as to the vibrator in the emitting atom, Richardson deduces a shift which is considerably larger than that observed.

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The second phenomenon of the change of frequency of line spectra is that of the Zeeman effect. Many lines show a simple Zeeman effect such as would be produced upon a vibrating negative electron. Other lines show a very complex Zeeman effect which as yet has not been fully explained. Still other lines show no Zeeman effect at all. All line spectra show a Zeeman effect that indicates that the vibrator carries a negative charge. Series lines usually show a similar resolution in a magnetic field as well as a similar behavior under variations of pressure, temperature, etc. Very important discussions of the Zeeman effect by Lorentz, Voigt, Ritz, etc., have recently appeared.

Some very interesting work has recently been done by Lenard,[2] Stark,[3] and others on the carriers of matter that are emitting light. In vacuum tubes, in arcs, in flames and in the radiations from radioactive bodies we have electrons, atoms, molecules, charged atoms or molecules or aggregations of these that are moving in some cases with very great velocities. The free electron, as we shall see, radiates a continuous spec-

[1] Phil. Mag., Nov., 1907.
[2] Ann. Phys., **9**, 642 (1902); **11**, 649 (1903); **13**, 475, 737 (1903).
[3] *Ibid.*, **14**, 506 (1904), etc.

trum, but the bound electron, being disturbed comparatively infrequently by collisions of the atom in which it is bound, will emit more or less monochromatic radiations. Now in the case of flames, arcs, etc., it is possible to separate the positively and negatively charged ions by means of an electric field.

Lenard's work indicated that the radiators of line spectra were either neutral atoms or positive ions, the principal series being due to neutral atoms, and the subordinate series to positively charged atoms. If an ion has a swarm of molecules about it, it is unable to radiate or absorb. Stark studied the Döppler effect of canal rays in vacuum tubes. He found that in the case of a beam of light coming from the canal rays in the same direction in which they are moving many spectrum lines showed a "rest" line and a displaced line due to the Döppler effect. He found that some series lines consisting of doublets originate from univalent positive ions and the mercury triplets start from divalent positive ions. Some lines show no Döppler effect and these originate from a negative electron joining a positive ion. The displaced line is separated from the normal line by a dark space which is found to be wider the smaller the wave length of the line. Assuming that there are particles of varying velocities in the canal rays, Stark concludes that a certain velocity is necessary before a particle begins to radiate light appreciably. Stark thus considers velocity of translation as one cause of radiation. The other cause of continuous radiation of energy by an atom is frequent collision with electrons or other charged atoms.

So far no satisfactory model has been devised that will act as a source of spectrum lines. No system that includes electrical charges in orbital motion is permanent on account of their radiation of energy. The favorite and best model consists of systems of coaxial circular rings of equidistant electrons, but even in this case Schott[1] has shown that such a model (in particular that of Nagaoka), although giving a

[1] Phil. Mag., April, 1908, p. 438.

large number of spectrum lines, is too unstable to produce wave trains of sufficient length.

Stark has recently suggested the possibility of explaining a positive charge as due to negative electrons revolving in circular orbits, the centers of these circular orbits being themselves on a circle. By means of such a device a positive charge can easily be explained. He thinks that line spectra originate from a system of this kind. The general trend[1] of opinion seems to favor the view that spectrum lines are due to some special mechanisms in the atom which are set in operation during ionization and operate for only a short time. At any one time the atom may be radiating light of but one frequency.

(*b*) *Spectra of Liquids and Solids.*—The optical phenomena of gases are so much better understood on account of our more perfect knowledge of gases that considerable space has been given to their discussion. On the other hand, the conditions in liquids and solids are so exceedingly complex that at present our theories are in the main very crude. Considerable advances in our experimental knowledge of these phenomena have recently been made and a short summary of these will be given.

The spectra of liquids and solids can be roughly divided into the continuous spectra emitted by very hot liquids or solids, secondary X-ray radiations, phosphorescent or fluorescent spectra and the absorption or emission of a banded spectra.

According to the present theory, X-rays, and possibly γ-rays, and the continuous spectra from hot liquids and solids are due to a rapid and irregular succession of sharp electromagnetic pulses, each of which is due to the change of velocity of electrons. Recent work on X- and γ-rays indicates that in most bodies a certain homogeneous secondary radiation is excited when the body is exposed to the X- and γ-rays. This secondary radiation seems very similar to the phosphorescent

[1] J. J. Thomson: "The Corpuscular Theory of Matter." 1907. Ladenburg and Loria: Nature, **79**, 7 (1908). Eagle: *Ibid.*, **79**, 68 (1908).

bands of the compounds investigated by Lenard and Klatt[1] and others. Lenard and Klatt[1] consider that electrons can exist in three different states—in a free state, as in the metals where they take part in conduction; a "liquid" state where there is a state of motion sensitive to light vibrations; and a "solid" state where the electrons take part in neither conduction nor the absorption of light. They consider that in the states of aggregation which cause phosphorescent bands there are certain places in the atoms, dynamids, where electrons can be stored at low temperatures. To each phosphorescent band there correspond then these phases: (1) an upper momentary or heat phase; (2) a permanent phase; (3) and a lower or momentary phase. For a great many bands they succeed in obtaining these three phases when they change the temperature sufficiently. The temperature of solid hydrogen is sufficiently low to bring most of the phosphorescent bands into the lower momentary phase. In this phase the electrons ejected from the metallic atom by photoelectric influence of illumination are fixed and stored in the neighborhood, only a few returning immediately, and these produce the "momentary light" observed during illumination. In the permanent phase the electrons are stored for a certain time in the dynamids and eventually return to the metallic atom.

Various theories have been proposed to explain the more or less general absorption throughout large regions of the spectrum. Drude[2] considers that in general ultraviolet bands are due to the absorption of electrons, and infrared bands to the absorption of ions. Houstoun,[3] Pfund[4] and others support this view.

(c) *Banded Spectra.*—By banded spectra we shall in general designate bands which at low temperatures become quite fine, such as the uranyl, neodymium or erbium bands. As the present paper deals with only a small range of temperature and concentration and but one solvent, a full review

[1] Ann. Phys., **15**, 451 (1904).
[2] *Ibid.*, **14**, 677–725, 936–961 (1904).
[3] P. Roy. Soc., Sept., 1909, p. 606.
[4] Astrophys. J., **24**, July, 1906.

of previous work will not yet be given. Rudorf[1] and Washburn[2] have given a very good review of this subject from the hydrate point of view.

Brewster observed, in 1831, that the transparency and color of many solids changes when they are heated. Schönbein, in 1852, states that many bodies become more highly colored at higher temperatures while at low temperatures they lose their color. He found that sulphur is colorless at —50° C. and bromine at —70° C. Moissan and Dewar, in 1903, found that fluorine becomes colorless at —253°, so that at low temperatures chlorine, bromine, iodine and fluorine are colorless.

Conroy (1891) found that the bands of cobalt glass are displaced towards the red with rise in temperature. Rizzo (1891) found similar results with glasses containing cobalt, didymium and manganese. Königsberger (1901) found the curve of absorption to be displaced towards the red with rise in temperature, but concluded that the maximum of absorption was not changed. This applied to the wider bands. The fine bands showed no displacement between 10° and 500° C. Hartley investigated the absorption spectra of a large number of solutions between 0° and 100°. He interpreted his results from the point of view of hydration. Houstoun investigated the bands of glasses containing uranium and neodymium but found no shifts of the bands.

Very important papers on this subject have been published by Becquerel, Ritz, Retschinsky, Stark, Bois and Elias, Königsberger and Kilchling, Page, Laub, Voigt, and others.

II. The Zeeman Effect.

An effort was made to obtain the Zeeman effect for the absorption bands of uranyl chloride and neodymium salt solutions. An account of the experimental arrangement was given in the introduction. At present no effect has been obtained, but it is hoped that in erbium solutions this may be possible. Most of the bands for which Becquerel found large

[1] Jahrb. Rad. u. Elek., **3**, 422 (1906); **4**, 380 (1907).
[2] *Ibid.*, **5**, 493 (1908); **6**, 69 (1909).

Zeeman effects were due to erbium. Besides it may be possible that the presence of foreign substances modifies the Zeeman effect.

III. Effect of Rise in Temperature on the Absorption Spectra.

In discussing the various spectrograms that show the effect of change in temperature on the absorption spectra of salts, these spectra will be divided into three kinds:

The first kind of absorption consists of wide bands, in many cases hundreds of A. U. wide. In many of the spectrograms only one edge of the band may appear, the other edge of it lying in parts of the spectrum to which the photographic film is not sensitive or to which the spectroscopic apparatus is not properly adapted. Examples of this kind of absorption are given by the copper or nickel salts, the ferricyanides, the chromates, etc. There is not the slightest indication of a finer structure to these bands.

The second kind of absorption spectra consists of diffuse bands that are quite narrow in many cases and are usually very weak at ordinary temperatures. These bands may be from ten to several hundred A. U. wide, and at very low temperatures may be broken up into finer and sharper bands. Examples of this kind of bands are the cobalt, uranyl or uranous bands. In many cases these bands appear only under very special conditions of concentration and depth of cell. If the amount of absorbing material is large, there is usually a wide absorption band in the region. This is well illustrated by the uranyl bands and the blue-violet band of the uranyl salts. If the amount of absorbing material is small, the transmission of light is so great that these faint bands are entirely obliterated.

The third class of bands are sharp and appear over rather wide ranges of concentration. They are exemplified by the neodymium and erbium bands. This classification of bands is quite suitable for the present article on account of the salts studied and the temperatures used. It is quite probable, however, that the latter two kinds of bands gradually merge into each other.

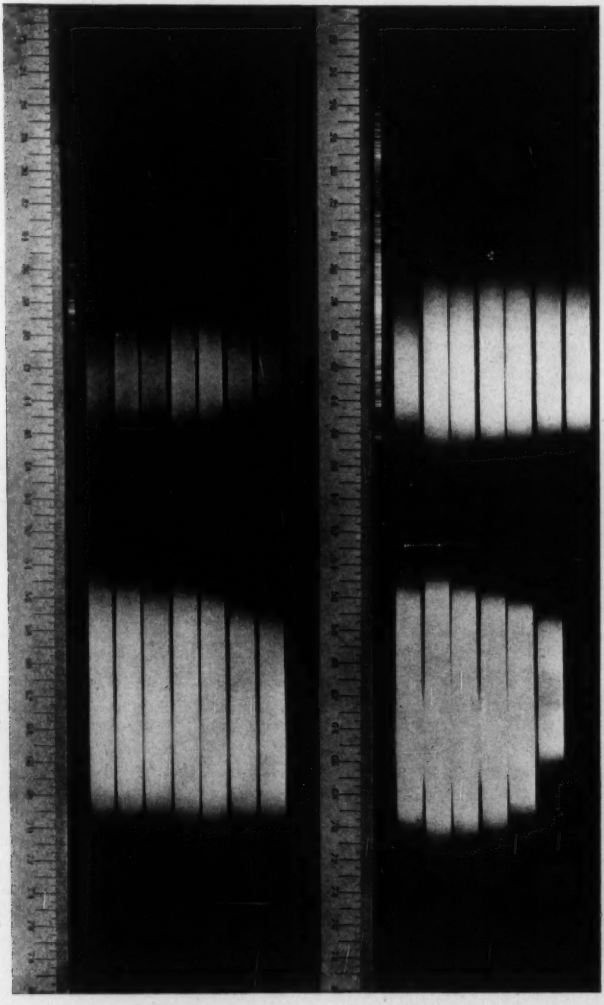
Cobalt Chloride.—A spectrogram, Plate IX, A, of the absorption spectrum of an aqueous solution of cobalt chloride was made for a 2.37 normal concentration and a depth of cell of 1.3 mm. The length of exposure was 3 minutes, current 0.7 ampere, and slit width 0.20 mm. Although there is transmission in the ultraviolet, no exposure was made to the spark in this instance, as this was the first salt worked with and the method of taking spectrograms had not as yet been fully perfected. Starting with the strip nearest the numbered scale, the temperatures were 1°.7, 14°, 30°, 45°, 56°, 72° and 81°.

At the lowest temperature there is an absorption band from λ 4800 to λ 5100. As the temperature rises this absorption band widens, slowly at first. At 56° it extends from about λ 4700 to λ 5600. At higher temperatures the increase in absorption in the red end of the spectrum is enormous and at 81° very little light is transmitted in this end, and for this reason the color of the solution becomes intensely blue. At 81° the absorption band runs from λ 4700 to λ 5700. From λ 5700 to λ 6000 there is a weak transmission. From λ 6000 on as far as the films are sensitive there is almost complete absorption. The bands $\lambda\lambda$ 6315 and 6440 appear at 72° and 81°. At lower temperatures the transmission is so great as to obscure these bands completely.

Several spectrograms were made of the absorption spectra of aqueous solutions of cobalt chloride of different concentrations. The time of exposure to the Nernst glower was the same for the three spectrograms, 3 minutes, the current being 0.7 ampere and the slit width 0.20 mm. The concentrations and depths of layer were as follows: 2.37 normal concentration, 1.3 mm. depth of layer and 2°, 15°, 30°, 45°, 58°, 73° and 81° (Plate IX, B); 0.315 normal concentration, the depth of layer 10 mm. and the temperatures —2°, 14°, 30°, 44°, 60°, 75° and 81°; 0.037 normal concentration, 83 mm. depth of layer and temperatures —0°.5, 14°, 30°, 45°, 60°, 70° and 81°.

The effect of concentration on the changes, due to rise in temperature in the absorption spectrum of a salt in solution,

Plate IX.



is brought out in these three spectrograms. For the most concentrated solution the yellow band at 2° runs from λ 4850 to λ 5400. There is a very intense action on the photographic film throughout the red. As the temperature rises the yellow band widens gradually and at 81° it extends from λ 4700 to λ 5700. At the higher temperature the whole red region is practically absorbed and the cobalt bands $\lambda\lambda$ 6100, 6250 and 6400 disappear. At 75° the cobalt bands showed faintly in a region of strong transmission between λ 5600 to λ 6650.

Cobalt Chloride and Aluminium Chloride.—A spectrogram, Plate X, A, was made to test the effect of rise in temperature on the change in the absorption spectra of a dilute solution of cobalt (0.00316 normal) in a concentrated 3.06 normal solution of aluminium chloride in water. The length of layer was 150 mm. The time of exposure was 2 minutes to the Nernst glower and 4 minutes to the spark. The current through the glower was 0.8 ampere and the slit width 0.20 mm. Starting with the strip adjacent to the comparison scale, the temperatures were 1°, 18°, 41°, 55°, 68° and 85°.

The effect of rise in temperature in this case was greater than in that of a more concentrated solution of cobalt chloride. There is absorption in the whole violet region, so that the spectrum at 1° consists simply of a transmission from λ 4000 to λ 6500. The transmission is weak from λ 6100 to λ 6500 and shows the cobalt bands at $\lambda\lambda$ 6100, 6350 (about 100 A. U. wide) and 6420. At 18° the transmission band runs from λ 4000 to λ 6050. With rise in temperature the transmission band narrows and at 85° extends only from λ 4300 to λ 6750. Weak bands about 100 A. U. wide appear at $\lambda\lambda$ 5050 and 5300. These are considerably broader at the lower temperatures.

Cobalt Chloride and Calcium Chloride.—A spectrogram, Plate X, B, was made to show the effect of rise in temperature on the absorption spectra of a 0.0095 normal cobalt chloride and 4.6 normal calcium chloride solution in water. The depth of the layer was 50 mm., the length of exposure to the Nernst glower 3 minutes, the current 0.7 ampere and the slit width 0.20 mm. The length of exposure to the spark was

5 minutes. The temperatures, starting with the strip adjacent to the comparison scale, were —1°.5, 20°, 30°, 45°, 57°, 74° and 88°.

The ultraviolet absorption reached to about λ 3000, with a great deal of general absorption throughout the violet. This general absorption increased slightly with rise in temperature. At —1°.5 there was transmission to λ 6900, and at 20° to λ 6800. At 20° and 30° the cobalt bands show quite strongly at $\lambda\lambda$ 6100, 6240, 6400. At 45° the absorption reaches to λ 6050, at 57° λ 5950, at 74° λ 5850 and at 88° λ 5800.

Wide bands appear at approximately λ 5000 and λ 5300. These bands are very weak, considerably weaker than for a solution of cobalt chloride and aluminium chloride.

Cobalt Sulphocyanate.—A spectrogram was made to show the effect of change of temperature on a 2-normal aqueous solution of cobalt sulphocyanate ($CoS_2C_2N_2$), 1 mm. deep. The length of exposure was 3 minutes to the Nernst glower, the current being 0.8 ampere and the slit width 0.20 mm. The length of exposure to the spark was 6 minutes. Starting with the strip nearest the comparison scale, the temperatures were 3°, 18°, 31°, 45°, 59° and 80°.

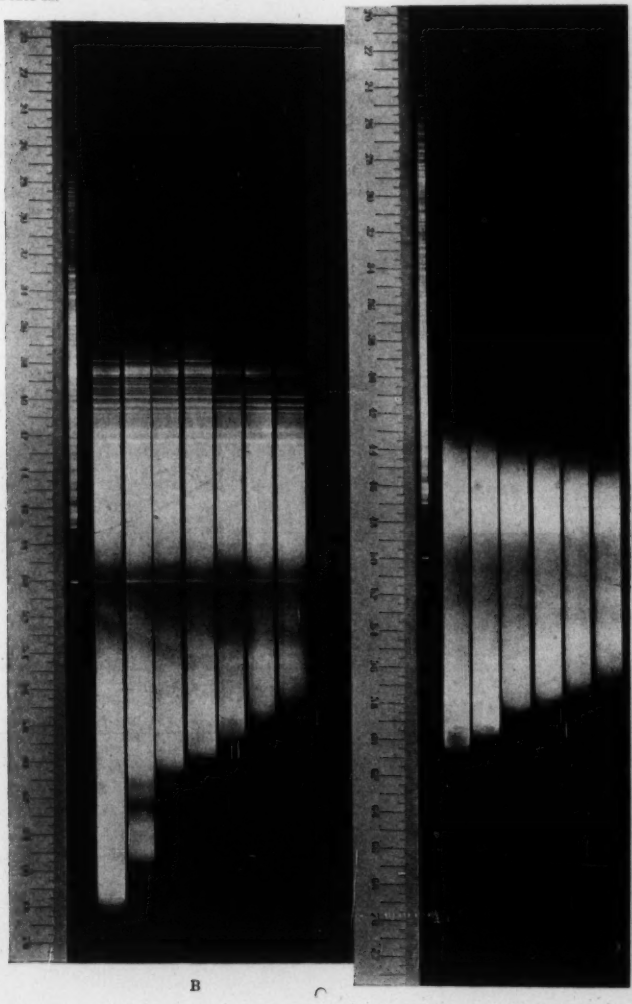
Under these conditions of concentration and depth of layer the cobalt sulphocyanate absorption consists of an ultraviolet absorption band and a wide band in the yellow and green. As the temperature is raised these bands both widen out on the red side. The effect of temperature is especially marked between 60° and 80°. The limits of the ultraviolet absorption are λ 3400 at 3°, λ 3450 at 18°, λ 3450 at 31°, λ 3500 at 45°, λ 3550 at 59°, and λ 3600 at 80°.

For the yellow-green band the limits are λ 4550 to λ 5600 at 3°, λ 4550 to λ 5630 at 18°, λ 4550 to λ 5650 at 31°, λ 4570 to λ 5700 at 45°, λ 4550 to λ 5750 at 59°, and λ 4550 to λ 6400 at 80°. At 59° there is a weak and broad band extending from λ 6000 to about λ 6300.

The remarkable feature of this spectrogram is that the yellow-green band widens only on the red side.

A spectrogram was made of a much more dilute solution of cobalt sulphocyanate in water, the concentration being

Plate X.



B C A

0.125 normal and the depth of cell 8 mm. The time of exposure to the Nernst glower with a current of 0.8 ampere and a slit width of 0.20 mm. was 2 minutes. The length of exposure to the spark was 6 minutes. Starting with the strip adjacent to the comparison spectrum, the temperatures were 6°, 20°, 33°, 47°, 59°, 73° and 80°.

In this spectrogram the effect of temperature on the absorption spectra of cobalt sulphocyanate was very small as compared with the effect on the 2-normal solution. At 6° the ultraviolet band absorbed pretty completely up to λ 3220. There was a slight transmission of light where a strong spark line was located, but this was small. The edge of the band was quite sharp. The yellow-green band extended from λ 4600 to λ 5500. At 80° the ultraviolet band has absorbed everything to λ 3300. The yellow-green band at this temperature runs from λ 4600 to λ 5600, showing a slight widening on the side of the longer wave lengths.

Nickel Acetate.—A spectrogram, Plate XI, A, was made of a 0.5 normal aqueous solution of nickel acetate, the depth of layer being 9 mm. The length of exposure to the Nernst glower was 2 minutes, and to the spark 6 minutes. The current in the glower was 0.8 ampere and the slit width 0.20 mm. Starting with the strip nearest the comparison spark, the temperatures were 6°, 23°, 38°, 52°, 64°, 74° and 84°.

The absorption spectrum of nickel acetate is characterized by a band in the violet and a slight absorption in the ultraviolet. At 6° the absorption in the ultraviolet is very small. At 84° it extends to about λ 2600. At 6° the violet band runs from λ 3800 to λ 4150. There is considerable transmission in this region at the lower temperatures. At the higher temperatures the limits of this band are $\lambda\lambda$ 3700 and 4400.

A spectrogram, Plate XI, B, of a 0.5 N solution of nickel acetate in water was made for various temperatures between 5° and 81°, the depth of layer being 3 mm.

At 5° there is almost complete transmission from λ 2300 to λ 7100. The only effect of rise in temperature was to increase slightly the absorption at the ultraviolet end of the

spectrum and to slightly weaken the transmission in the region λ 4000.

Nickel Sulphate.—A spectrogram was made of the absorption spectra of a 2-normal aqueous solution of nickel sulphate 3 mm. deep. The length of exposure to the Nernst glower was 2 minutes and to the spark 6 minutes. The current through the glower was 0.8 ampere and the slit width 0.20 mm. Starting with the strip nearest the comparison spectrum the temperatures were 5°, 19°, 32°, 47°, 61°, 72° and 81°.

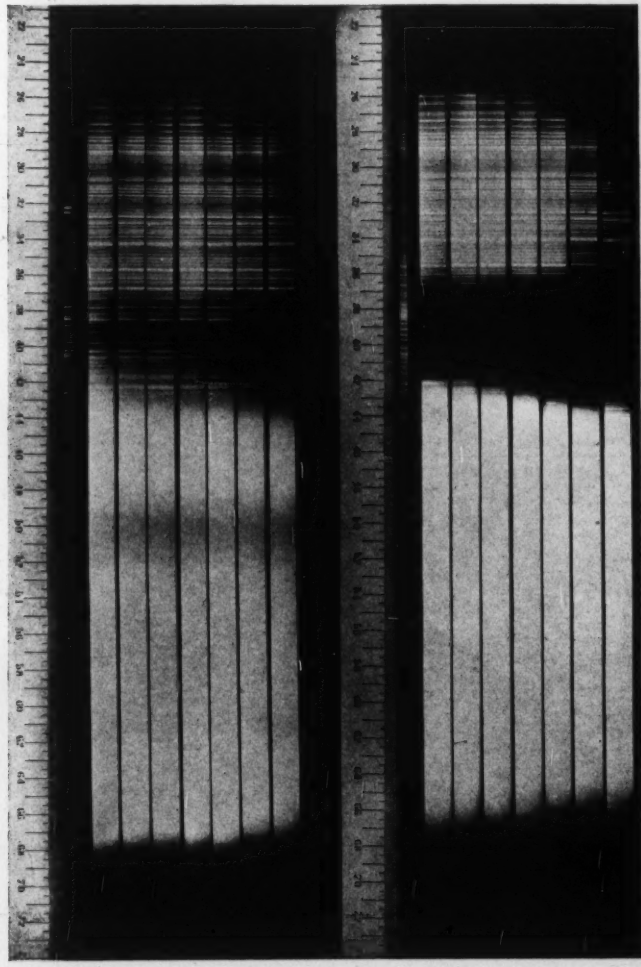
Nickel sulphate is remarkable for the fact that it has practically no absorption in the ultraviolet. The violet band at 5° extends from λ 3700 to λ 4200 and at 81° from λ 3700 to λ 4350. It will thus be seen that the effect of temperature upon the absorption spectrum of nickel sulphate is very small and consists simply in the violet band widening slightly in the direction of the red.

Copper Bromide.—The two spectrograms, Plate XII, showing the absorption spectra of copper bromide in water for various temperatures were made for different concentrations of the salt. A gives the absorption of a 2.06 normal solution 1 mm. thick and B the absorption of a 0.25 normal solution 8 mm. thick. The time of exposure to the Nernst glower was 2 minutes (current 0.8 ampere and slit width 0.20 mm.) and to the spark 6 minutes. Starting with the strip nearest the comparison scale, the temperatures at which exposures were made for A were 6°, 17°, 30°, and 45°; for B 6°, 17°, 31°, 46°, 59°, 71° and 85°.

As the spectrograms show, the effect of change in temperature on the absorption spectrum is very marked. Above 45° the concentrated solution did not transmit enough light to affect the photographic film.

Chromium, Calcium and Aluminium Chlorides.—A, Plate XIII, represents a spectrogram showing the effect of rise in temperature on an aqueous solution of chromium and aluminium chlorides. The concentration of the chromium chloride was 0.125 normal, and that of the aluminium chloride 2.28 normal. The depth of layer was 9 mm. The length of

Plate XI.



B A

Plate XII.

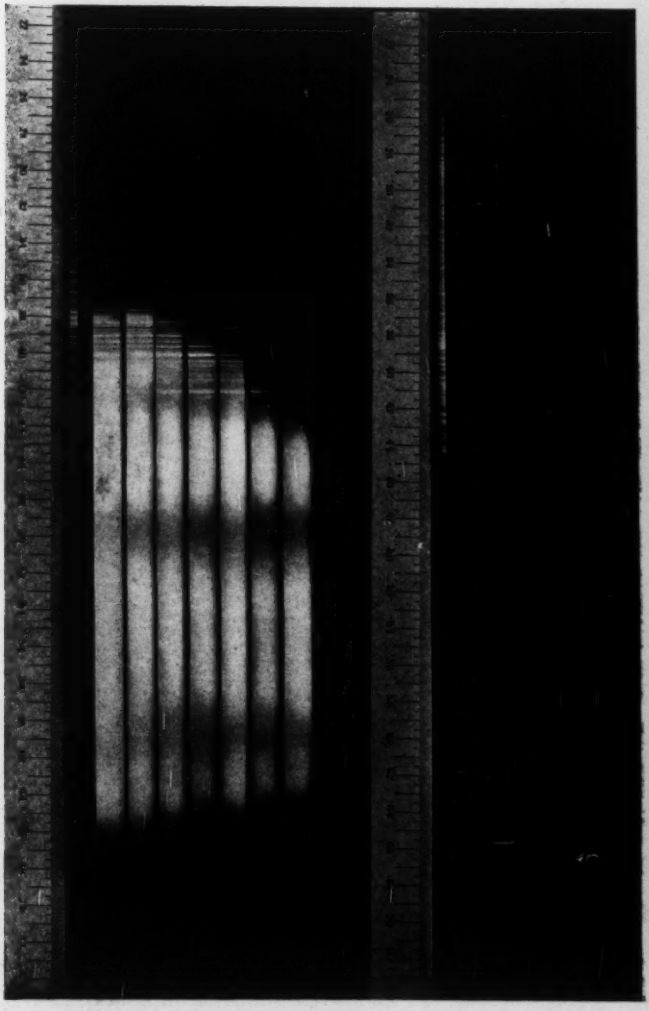
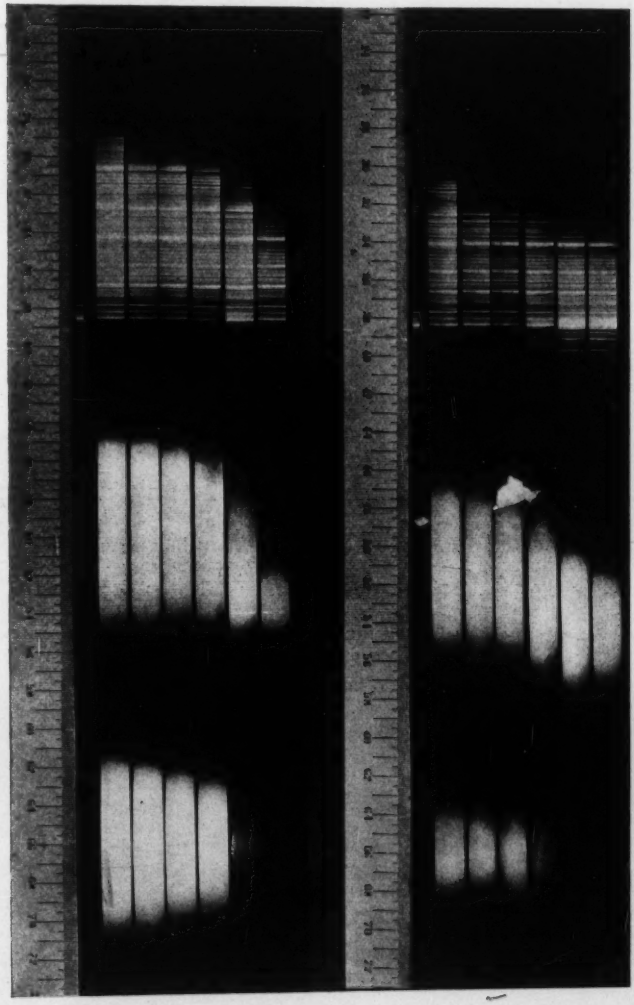


Plate XIII.



exposure to the Nernst glower was 4 minutes (current 0.8 ampere and slit width 0.20 mm.) and to the spark 6 minutes. Starting with the strip adjacent to the comparison scale, the temperatures were 6°, 19°, 36°, 51°, 66° and 81°.

The most marked effect of the aluminium chloride was the production of a very pronounced unsymmetrical broadening which does not occur when a pure aqueous solution of chromium chloride is heated. At 6° the ultraviolet band extends to λ 3000, at 81° to λ 3300, a much greater widening than takes place for a chromium chloride solution in water. At 6° the blue-violet band extends from λ 4100 to λ 4600 and the yellow band from λ 5800 to λ 6200. Not only do the red sides of the blue-violet and yellow bands widen out enormously towards the red, but the short wave-length edges of these bands actually move towards the red. This effect is much more pronounced in the changes in temperature from 51° to 66° and from 66° to 81°. At 81° the blue-violet band extends from λ 4150 to λ 5050 and the yellow band from λ 5900 throughout the remaining portion of the spectrum, as far as the film is sensitive. The fine chromium bands in the red do not appear.

B, Plate XIII, is a spectrogram giving the absorption spectrum of a 0.125 normal solution of chromium chloride and a 3.45 normal solution of calcium chloride in water at different temperatures. The depth of the solution was 9 mm., the length of the exposures to the Nernst glower 5 minutes and to the spark 6 minutes. The current through the glower was 0.8 ampere and the slit width 0.20 mm. Starting with the strip adjacent to the comparison scale, the temperatures at which the exposures were made were 6°, 19°, 31°, 45°, 64° and 80°.

The effect of rise in temperature on the absorption spectrum of a mixture of chromium chloride and calcium chloride is very similar to the effect on the mixture of chromium chloride and aluminium chloride. The blue-violet and the yellow bands widen unsymmetrically, and the short wave-length edges of these bands apparently move towards the red at the higher temperatures.

At 6° the ultraviolet band extends to λ 2800, the blue-violet band from λ 4000 to λ 4400 and the yellow band from λ 5600 to λ 6100. At 64° the ultraviolet band extends to λ 3100, the blue-violet band from λ 4000 to λ 4600 and the yellow band from λ 5650 to λ 6300. At 80° the ultraviolet band extends to λ 3250, the blue-violet band from λ 3950 to λ 5000 and the yellow band from λ 5700 throughout the red end of the spectrum as far as the film is sensitive.

Uranyl Chloride.—A spectrogram, A, Plate XIV, was made of the absorption spectrum of a normal aqueous solution of uranyl chloride, the depth of cell being 3 mm. Exposures were made to the Nernst glower for 90 seconds (current 0.8 ampere and slit width 0.20 mm.). The time of exposure to the spark was 6 minutes. Starting from the comparison spectrum, the temperatures were 6°, 18°, 34°, 52°, 68° and 82°.

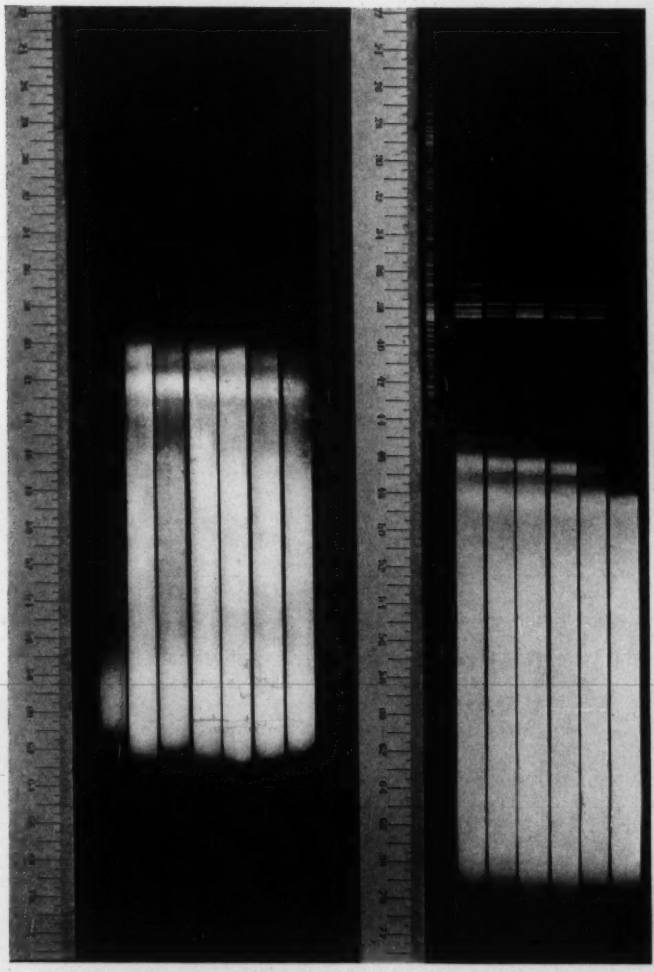
At 8° the ultraviolet band extended to λ 3550, the blue-violet band from λ 4000 to λ 4450. The bands *a*, *b* and *c* appeared, but the *a* band is very faint. The wave lengths of the *b* and *c* bands were $\lambda\lambda$ 4565 and 4725.

At 82° the ultraviolet band extends to λ 3700, and the blue-violet band from λ 3950 to λ 4600. At this temperature only the *b* band appears, *a* being very weak and *c* completely merged into the blue-violet absorption band. The *b* band is located at λ 4755.

A spectrogram, B, Plate XIV, was made of a 0.0156 normal aqueous solution of uranyl chloride 196 mm. deep. Exposures were made to the Nernst glower for 30 seconds (current 0.8 ampere and slit width 0.20 mm.). No exposures were made to the spark except for comparison spectra. Starting with the numbered scale, the temperatures were 6°, 18°, 29°, 44°, 59°, 71° and 79°.

For this concentration there is a very slight temperature effect. There is a very faint transmission band between the ultraviolet and blue-violet bands. This is extremely faint and is practically unaffected by temperature. The blue-violet band widened slightly with rise in temperature. The uranyl bands in the concentrated solution were much stronger and wider than in the dilute solution.

Plate XIV.



B A

Uranyl Nitrate.—A spectrogram was made of a 0.0156 normal uranyl nitrate solution in water, the depth of layer being 196 mm. Exposures were made to the Nernst glower for 30 seconds, the current being 0.8 ampere and the slit width 0.20 mm. The length of exposure to the spark was 4 minutes. Starting with the strip nearest the scale, the temperatures were 9°, 23°, 46°, 59°, 70° and 79°.

At 9° the ultraviolet absorption band extended to λ 3430. Throughout the blue-violet band there was considerable transmission at this temperature, the stronger spark lines being only partially absorbed. The *a*, *b* and *c* bands appeared, all being extremely weak, however, and in quite striking contrast with their strength in the aqueous solutions investigated in the earlier part of the work. Their wave lengths were $\lambda\lambda$ 4550, 4705 and 4870.

As the temperature was raised, both the ultraviolet and the blue-violet bands widened. The intensity of the uranyl bands, on the other hand, did not seem to vary with the temperature. At 79° the ultraviolet band extends to λ 3550. The blue-violet band extends from λ 3900 to λ 4450. Only the *a* and *b* bands appear at this temperature, their positions being λ 4710 and λ 4875. There may be a slight shift towards the red, but if there is, it is too small in amount to be established with certainty.

Uranyl Acetate.—A spectrogram showing the effect of rise in temperature was made for a 0.0039 normal aqueous solution of uranyl acetate 196 mm. deep. The exposures were made for 30 seconds to the Nernst glower, with a current of 0.8 ampere and a slit width of 0.20 mm. No exposure was made to the spark at all. The temperatures, starting with the strip nearest the comparison spectrum, were 6°, 18°, 30°, 43°, 56°, 68° and 75°.

The spectrogram shows the ultraviolet and blue-violet bands common to all uranyl salts. The transmission band between these absorption bands is about 200 A. U. wide and changes very little with change in temperature. The blue-violet band advances rapidly towards the red as the temperature rises. At 6° the blue-violet band extends from λ 3950

to λ 4500. The latter edge gradually runs towards the red until at 75° it is about λ 4600. The uranyl bands *a* and *b* appear. These are very weak and gradually shift towards the red with rise in temperature.

Uranous Chloride.—To a normal solution of uranyl chloride in water was added a small amount of hydrochloric acid and zinc. The production of hydrogen reduced the uranyl to the uranous state. The same can be done in some cases by simply passing hydrogen gas through the uranyl solution. The solution was placed in the glass trough and a temperature run made as in the usual manner. The thickness of layer was 1 mm. The length of exposure was 50 seconds to the Nernst glower and 4 minutes to the spark, the current through the glower being 0.8 ampere and the slit width 0.20 mm. Starting with the strip nearest the comparison scale, the temperatures were 8°, 17°, 33°, 48°, 62° and 73°. An exposure was also made at 80° which is not shown in the spectrogram B.

At 8° a mist formed on the prisms and for this reason the spectrum film taken at this temperature is much underexposed and the bands appear wider than at the higher temperatures. At this temperature there is complete absorption of the shorter wave lengths to λ 3650. A blue-violet absorption extends between λ 4050 and λ 4450. Following this band are three strong bands of about equal intensity and each almost 100 A. U. wide. Their wave lengths are approximately $\lambda\lambda$ 4590, 4760 and 4970. Following is a band at λ 5500, a wide band from λ 6400 to λ 6630 and a rather narrow band at λ 6740.

The absorption does not change very greatly until a temperature of 60° is reached. About this temperature the increase in absorption is quite rapid as the temperature rises. At 73° the ultraviolet band has widened to λ 3800, the blue-violet band covers the region from λ 4050 to λ 5000. The bands $\lambda\lambda$ 4600, 4770 and 4980 at 8° have shifted slightly to the red with rise in temperature.

None of the other bands seem to shift to the red at all and the broadening seems to be quite symmetrical. The band at λ 5500 has become about twice as wide as it was at the

lower temperatures, and the two red bands have merged into one band running from λ 6350 to λ 6800. Between 73° and 80° the absorption increases very greatly. All short wave lengths are absorbed up to λ 5050. The band in the green runs from λ 5450 to λ 5600 and the band in the red has also widened very greatly, extending from λ 6200 to λ 6800.

Uranyl Sulphate.—A spectrogram was made for a normal solution of uranyl sulphate, the depth of cell being 3 mm. The time of exposure was 90 seconds to the Nernst glower with a current of 0.8 ampere and a slit width of 0.20 mm. The time of exposure to the spark was 6 minutes. Starting with the strip nearest the numbered scale, the temperatures were 5°, 19°, 32°, 54°, 67° and 84°.

The rise in temperature from 5° to 84° caused an encroachment of the ultraviolet band into the regions of greater wave length. The blue-violet band increased in width, especially towards the red, as the temperature was raised. The uranyl bands themselves changed very slightly in intensity with rise in temperature.

At 5° the ultraviolet was absorbed to λ 3500. The blue-violet band extended from λ 3900 to λ 4400. The uranyl bands *a*, *b* and *c* appeared at $\lambda\lambda$ 4570, 4730 and 4910.

At 84° the ultraviolet band extended to λ 3600, the blue-violet band from λ 3850 to λ 4550. The bands *a*, *b* and *c* have become considerably more diffuse. Their positions are $\lambda\lambda$ 4590, 4745 and 4925, approximately.

Uranyl Sulphate.—A much more dilute solution (0.0156 normal) of uranyl sulphate (Plate XV, B), containing approximately the same amount of salt as the concentrated solution, was used. The length of cell in this case was 196 mm. The exposure was for 30 seconds to the Nernst glower (current 0.8 ampere, slit width 0.20 mm.). The time of exposure to the spark was 4 minutes. Starting with the strip next the comparison scale, the temperatures were 6°, 19°, 36°, 51°, 67° and 81°.

At 6° the ultraviolet band extends to λ 3500, and the blue-violet band from λ 3950 to λ 4450. The positions of the *a*, *b* and *c* bands are $\lambda\lambda$ 4565, 4720 and 4895. At 81° the ultra-

violet absorption extended to λ 3600 and the blue-violet band from λ 3900 to λ 4500. The *a* and *b* bands were located at $\lambda\lambda$ 4735 and 4915. The effect of concentration upon the temperature coefficient seems to be very small. In both concentrations, as the temperature was increased there was a slight shift of the uranyl bands to the red.

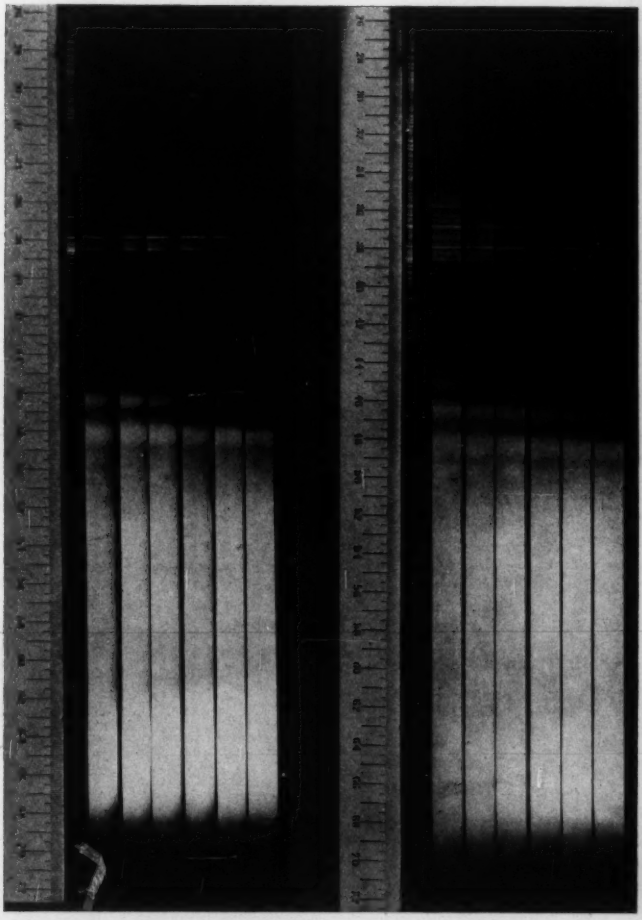
Praseodymium Chloride.—A spectrogram, Plate XVI, A, was made of a 2.56 normal aqueous solution of praseodymium chloride 3 mm. deep. Exposures were made to the Nernst glower (current 0.8 ampere and slit width 0.20 mm.) for 20 seconds. The time of exposure to the spark was 4 minutes. Starting with the strip nearest the numbered scale, the temperatures were 7°, 23°, 40°, 52°, 68° and 84°.

The ultraviolet is absorbed up to λ 2700 and this absorption does not vary greatly with temperature, increasing slightly, however. At 7° there are bands from λ 4385 to λ 4500, λ 4640 to λ 4720, λ 4810 to λ 4845, λ 6860 to λ 6990. This latter band is double, the red component being much the narrower and having its center at λ 6980. Throughout the remainder of the spectrum there is complete transmission.

At 84° the absorption bands are located at $\lambda\lambda$ 4380 and 4510, $\lambda\lambda$ 4640 and 4730, $\lambda\lambda$ 4810 and 4845, and $\lambda\lambda$ 6870 and 6775. The bands all widen slightly except the latter. At 7° the latter band consisted of two separate bands. At 84° the λ 6980 band has diffused into the other band and the general transmission throughout the band has been greatly increased. In this respect this band is very peculiar indeed, and behaves with respect to temperature changes in just the opposite way from practically all other bands investigated.

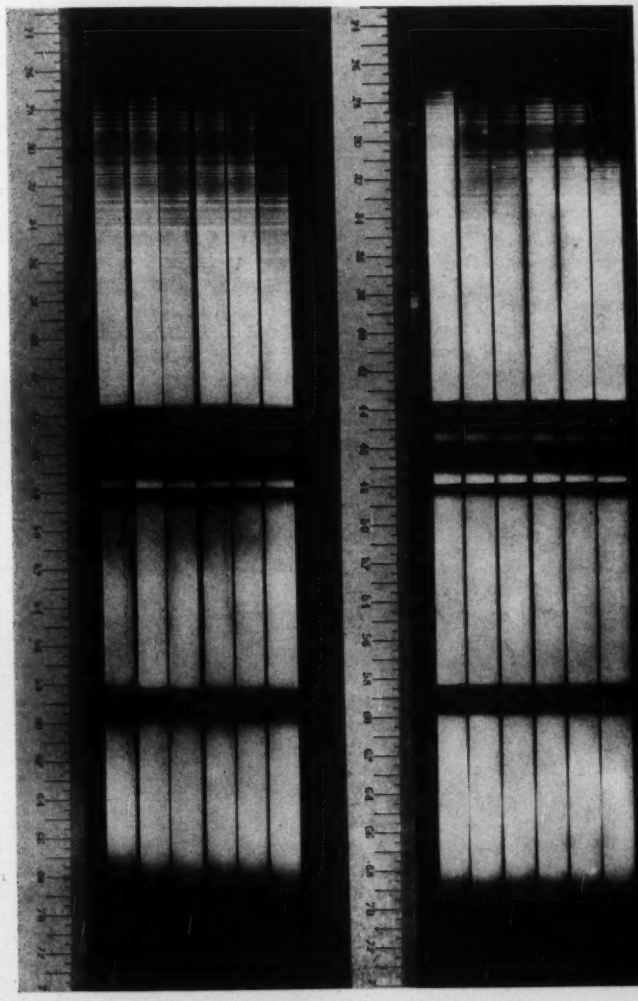
Praseodymium Chloride.—A spectrogram, Plate XVI, B, was made of a 0.043 normal aqueous solution of praseodymium chloride 196 mm. deep. This spectrogram was to show whether changes due to temperature in the spectrogram were affected by the concentration of the solution. The length of exposure to the Nernst glower (current 0.8 ampere and slit width 0.20 mm.) was 20 seconds. The length of exposure to the spark was 4 minutes. Starting with the strip nearest

Plate XV.



B A

Plate XVI.



B A

the comparison spectrum, the temperatures were 7°, 20°, 36°, 51°, 66° and 82°

The absorption spectrum of the dilute solution is practically the same as that for the concentrated solution. At 7° bands occur from λ 4385 to λ 4490, λ 4640 to λ 4715, λ 4810 to λ 4840, λ 5860 to λ 5940 and a narrower band at λ 5980.

The ultraviolet absorption at 7° extends to λ 2650, at 82° it extends to λ 2750. The other bands are at $\lambda\lambda$ 4385, 4490, $\lambda\lambda$ 4650, 4715, $\lambda\lambda$ 4805 to 4835, $\lambda\lambda$ 5870 to 5930. The band λ 5980 has become much more diffuse. The band adjacent to it has also become narrower and much more filled up by general transmission than at the lower temperatures. It will be seen in general that there is very little, if any, temperature change in the absorption bands of praseodymium chloride at this concentration, except the bands in the red, which become narrower and weaker at the higher temperatures. In the concentrated solution the change in this band was not as great as in the dilute solution. In the concentrated solutions the other bands widened slightly more than they do in the solution here described.

Praseodymium Nitrate.—A spectrogram, Plate XVII, A, showing the effect of rise in temperature was made for a 2.6 normal aqueous solution of praseodymium nitrate 46.5 mm. deep. The exposures were made to the Nernst glower (current 0.8 ampere and slit width 0.20 mm.) for 20 seconds. The length of exposure to the spark was 4 minutes. Starting with the strip nearest the comparison scale, the temperatures were 6°, 19°, 47°, 70° and 90°.

On account of the great concentration and the depth of cell, the absorption bands are very wide. The whole ultraviolet portion of the spectrum is absorbed up to λ 3550. Rise in temperature does not cause any change in this absorption. The band in the blue extends from λ 4300 to λ 4940 at 6°. A weak and rather broad band appears at λ 5120 and a narrow band at λ 5240, this band being about 15 A. U. wide. The yellow band extends from λ 5760 to λ 6120 at 6°.

As the temperature rises the blue and yellow bands gradually widen. At 47° the blue band extends from λ 4290 to

λ 4950, the yellow band from λ 5750 to λ 6120. At 90° the violet band was bounded by $\lambda\lambda$ 4280 and 4960, the yellow band by $\lambda\lambda$ 5740 and 6140. At 70° the ballast burned and the exposure to the Nernst glower was not quite as long as it should have been.

The bands $\lambda\lambda$ 5120 and 5240 appeared very slightly affected by the rise in temperature here used. The violet and yellow bands broadened very slightly with rise in temperature and broadened symmetrically.

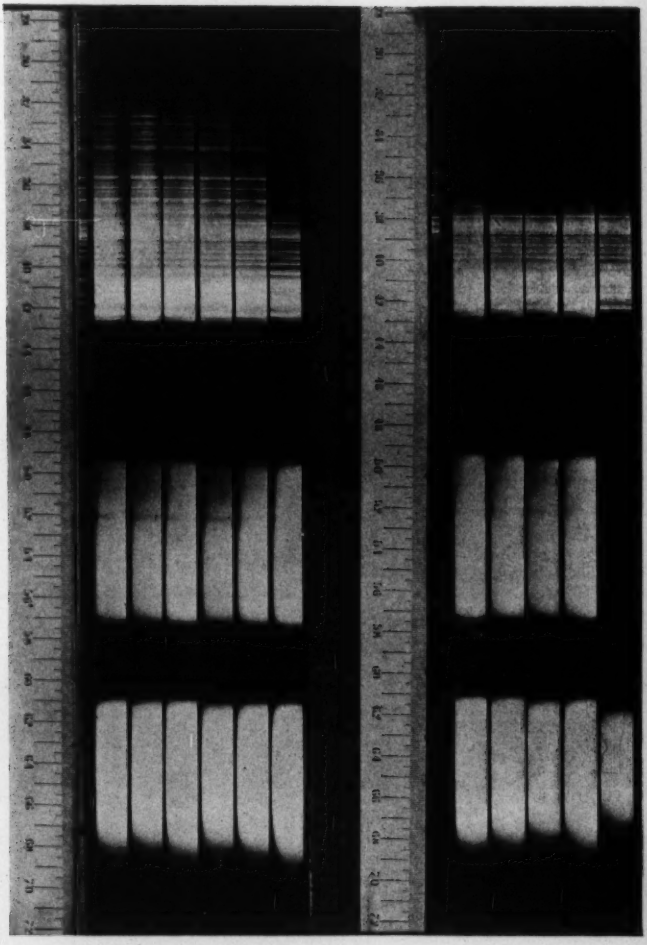
Plate XVIII, A, represents the absorption spectra of a 2.6 normal solution of praseodymium nitrate 3 mm. deep. Starting with the strip nearest the numbered scale, the temperatures are 6°, 16°, 34°, 46°, 58°, 70° and 82° C.

The four characteristic wide absorption bands appear very slightly affected by rise in temperature. The NO_3 band in the ultraviolet widens slightly.

Praseodymium Chloride.—This spectrogram, Plate XVIII, B, of an aqueous solution of praseodymium chloride shows the effect of change of temperature between 7° and 84° on a 2.56 normal solution 48.00 mm. deep. The exposure to the Nernst glower (current 0.8 ampere and slit width 0.20 mm.) was for 20 seconds. The exposure to the spark was for 4 minutes. Starting from the comparison spectrum, the strips were taken at the temperatures 7°, 20°, 35°, 51°, 66° and 84°.

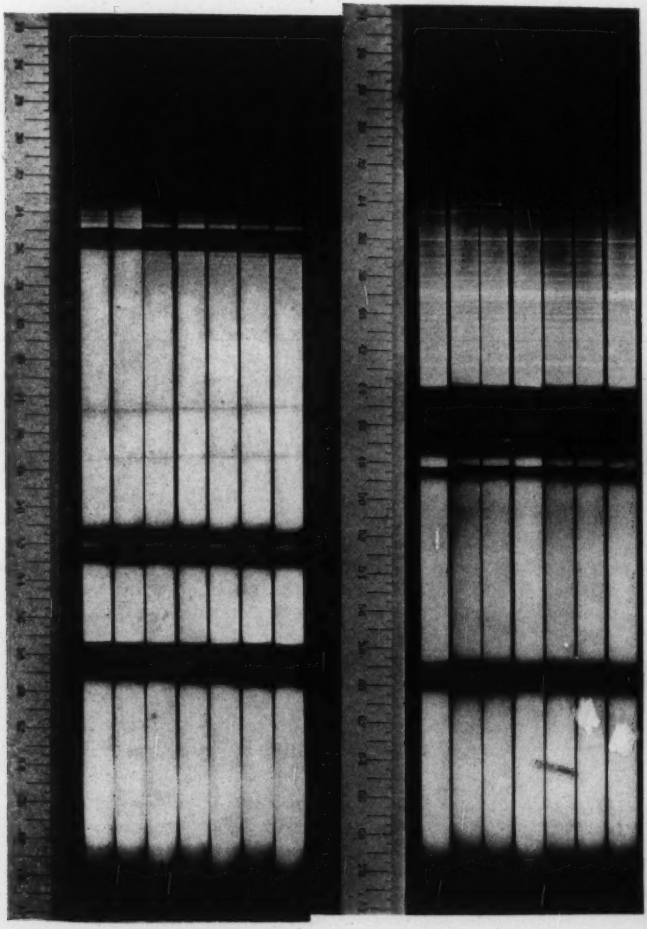
The spectrum strip taken at 7° shows a large band in the blue and one in the yellow. There is absorption in the ultraviolet. In the case of praseodymium nitrate the absorption in the ultraviolet was probably due to the NO_3 band. This absorption was found to be unaffected by temperature. In the case of praseodymium chloride the absorption increases very markedly with rise in temperature. At 7° the limits of the blue band are $\lambda\lambda\left\{\begin{matrix}4280\\4270\end{matrix}\right\}$ and $\left\{\begin{matrix}4940\\4930\end{matrix}\right\}$ and for the yellow band $\lambda\lambda$ 5750 and 6100. There is slight absorption in the region λ 5000 to λ 5100, which is probably due to absorption bands. Two fine bands, each about 8 A. U. wide, appear at $\lambda\lambda$ 5220 and 5235. Absorption of the shorter wave lengths

Plate XVII.



B A

Plate XVIII.



B A

at 7° is complete to λ 3100, at 51° λ 3200, and at 84° λ 3300. At 51° the blue band is located at $\lambda\lambda$ 4280 and 4950, and the yellow band at $\lambda\lambda$ 5740 and 6110.

At 84° the limits of the blue band are $\lambda\lambda$ 4280 and 4950, and of the yellow band $\lambda\lambda$ 5750 and 6110. The widening of the bands is very small indeed. The fine bands $\lambda\lambda$ 5220 and 5235 become much more diffuse and at the higher temperatures could not be resolved at all. At 7°, however, the two bands were entirely separated. The blue and yellow bands are very slightly affected by temperature within the ranges investigated.

Neodymium Chloride.—A spectrogram, Plate XX, A, of a 3.4 normal solution of neodymium chloride in water, 43 mm. deep, was taken. The exposures were made for 3 minutes to the Nernst glower, the current being 0.8 ampere and slit width 0.20 mm. The time of exposure to the spark was 6 minutes. Starting with the strip nearest to the comparison spark, the temperatures were 6°, 21°, 36°, 47°, 60°, 77° and 83°.

Neodymium chloride, under the conditions of this experiment, gives a complete absorption in the ultraviolet up to λ 3700. From λ 3700 throughout the violet and blue regions there is almost complete general absorption, this general absorption increasing with the temperature. A band of absorption seems to appear at about λ 4000, but this is somewhat doubtful. A very sharp and strong band appears at λ 4185. A band occurs at $\lambda\lambda$ 4265, 4305 and one at $\lambda\lambda$ 4320 and 4350. The transmission band between these two bands is faint and disappears at 77°. An absorption band extends from λ 4380 to λ 4520 and there is then complete absorption up to λ 4980. The transmission between these bands is very weak and has almost disappeared at 83°. Between $\lambda\lambda$ 4970 and 5365 there is an absorption band, the long wave-length edge of this band being extremely sharp. A similar band lies between $\lambda\lambda$ 5620 and 6000. Next comes a series of five absorption bands. The first of these is 20 A. U. wide and is at λ 6250, the next is 10 A. U. wide and is at λ 6270. The bands $\lambda\lambda$ 6295 and 6315 almost touch each other, the distance between them being

but two or three A. U. The last band is about 30 A. U. in width and its center lies at λ 6380. The last band that could be photographed was between λ 6720 and λ 6965.

The effect of rise in temperature is quite evident, most of the bands widening and their sharpness gradually decreasing. At 83° the band $\lambda\lambda$ 4970–5365 described above has widened to $\lambda\lambda$ 4960 and 5395, the widening being slightly greater on the red side. The band $\lambda\lambda$ 5620 to 6000 has widened to $\lambda\lambda$ 5610 and 6050, this widening also being unsymmetrical. The five bands in the vicinity of λ 5800 at 6° have merged into three bands. The red band is at $\lambda\lambda$ 6720 to 6990. It will thus be seen that the widening is in general greater on the red side of the bands.

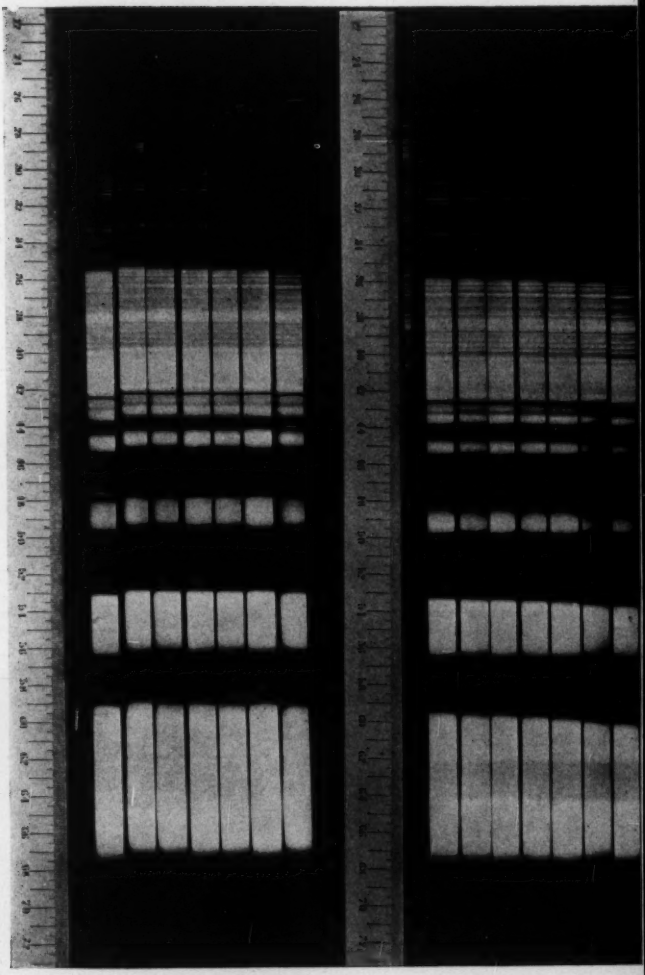
Neodymium Nitrate.—A spectrogram, Plate XX, B, was made of a 2.96 normal aqueous solution of neodymium nitrate 38.5 cm. deep. An exposure of 3 minutes was made to the Nernst glower, the current being 0.8 ampere and the slit width 0.20 mm. The length of exposure to the spark was 6 minutes. Starting with the strip nearest the comparison scale the temperatures were 7°, 17°, 30°, 44°, 59°, 70° and 82°.

At 7° there is practically complete absorption in the ultraviolet up to λ 4600, due to the absorption of the NO_3 group. The edge of the band is very sharp. Other bands are as follows: λ 4270 to λ 4288, λ 4386 to λ 4500, λ 4538 to λ 4870, λ 4970 to λ 5370, λ 5620 to λ 6005, λ 6240 to λ 6270, and λ 6705 to λ 6970.

It should be noticed here that the absorption spectrum of neodymium nitrate under the present conditions is quite different from the absorption of a similar solution of neodymium chloride. In the case of the chloride there was a very great amount of absorption throughout the ultraviolet and violet portions of the spectrum. In the case of the nitrate there is almost complete absorption up to λ 3600 and from that wave length to λ 4270 there is complete transmission. In this region appeared several narrow and sharp bands in the neodymium chloride absorption spectrum.

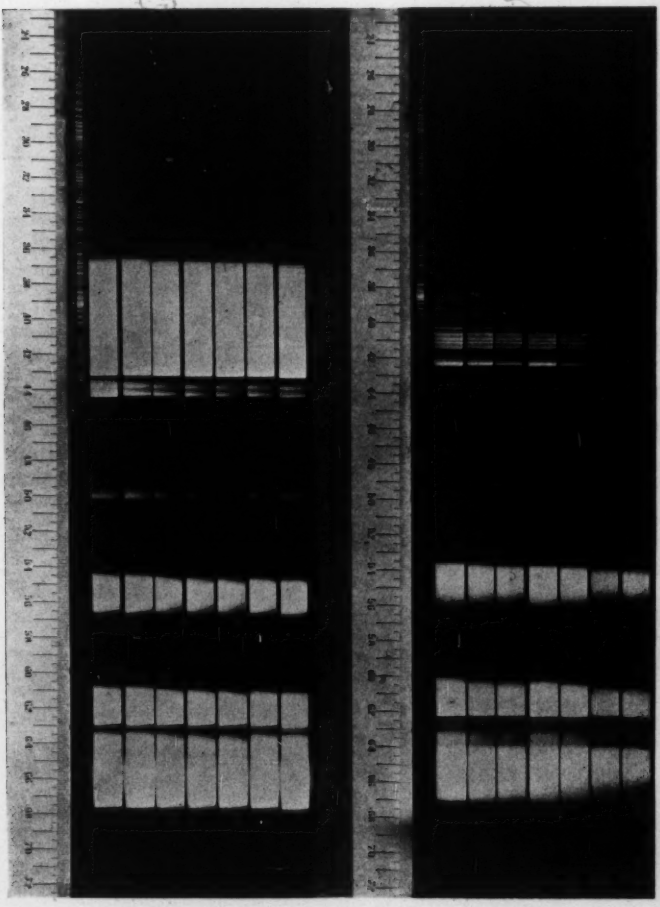
From the spectrum shown in the upper strip and for which

Plate XIX.



B A

Plate XX.



B A

the temperature was 82° we see that the NO_3 band extends to λ 3615. The band λ 4274 has become about 5 A. U. wider than it was at 7°. A wide and weak band appears at λ 4350 and this is considerably stronger than at the lower temperatures. The positions of the other bands are: λ 4380 to λ 4560, λ 4535 to λ 4870, λ 4970 to λ 5390, λ 5615 to λ 6025 and λ 6700 to λ 6970. The increase in width of these bands due to increasing the temperature from 7° to 82°, is 60, 20, 25 and about 0 A. U., respectively.

Plate XVIII, B, represents the absorption spectra of a 2.15 normal solution of neodymium nitrate 3 mm. deep. Starting with the strip nearest the numbered scale, the temperatures were 4°, 17°, 29°, 44°, 58°, 71° and 84°.

As the temperature rises the NO_3 band widens slightly. The bands in the region of λ 3500 become more diffuse and slightly wider. The same is true of the bands at λ 5200. The broad band at λ 5800 widens, especially on the long wavelength edge.

Neodymium Salts.—A spectrogram, A, Plate XIX, of the absorption spectrum as affected by change in temperature was made for a neodymium chloride solution in water, the concentration being 3.4 normal and the depth of layer 12 mm. The length of exposure was 2 minutes to the Nernst glower (current 0.8 ampere and slit width 0.20 mm.). The time of exposure to the spark was 6 minutes. Starting with the strip nearest the numbered scale, the temperatures were 11°, 22°, 33°, 45°, 59°, 73° and 85°.

At 11° an absorption band appears at about λ 2970, a very strong band from λ 3250 to λ 3285, and an adjacent band from λ 3285 to λ 3310. A very narrow and feeble transmission band separates these two bands. At 85° the transmission band has weakened very much. At 11° a very strong band lies between λ 3490 and λ 3580. The band λ 4274 is about 8 A. U. wide. An extremely narrow band appears at λ 4297, λ 4306 and λ 4324. At λ 4234 is a wider and rather diffuse band, it being about 12 A. U. wide. Bands lie between $\lambda\lambda$ 4415 and 4470, $\lambda\lambda$ 4580 and 4650, $\lambda\lambda$ 4665 and 4710, $\lambda\lambda$ 4740 and 4775, $\lambda\lambda$ 4815 and 4835, and the very wide bands $\lambda\lambda$ 5010

and 5300 and $\lambda\lambda$ 5665 and 5935. Weak bands are located at λ 4645, λ 4800, λ 5320, λ 6235, λ 6255, λ 6280, λ 6305 and λ 6380. Rather diffuse bands appear at $\lambda\lambda$ 6780 and 6840, at λ 6850 and from λ 6870 to λ 6920.

The effect of rise in temperature from 11° to 85° is quite noticeable, although it is not great. In the ultraviolet there is a slight increase in the general absorption. The band $\lambda\lambda$ 3285 and 3310 widens slightly. The band $\lambda\lambda$ 3490–3580 at 11° has widened so that at 85° it extends from λ 3450 to λ 3600. The band at $\lambda\lambda$ 4415 and 4470 has widened but little. The bands from λ 4600 to λ 4800 have also widened but little. The faint diffuse bands $\lambda\lambda$ 4645 and 4800 have practically disappeared. The bands $\lambda\lambda$ 5010 and 5300 and $\lambda\lambda$ 5665 and 5935, at 11°, have widened at 85° to $\lambda\lambda$ 5010 and 5350 and $\lambda\lambda$ 5660 and 5985. The widening of the latter band is distinctly unsymmetrical. The existence of the band λ 5320 causes the band λ 5010 to λ 5300 to widen unsymmetrically.

The bands in the region λ 6300 become less sharp as the temperature rises. At 11° there was considerable transmission in the region λ 6850. At 85°, however, this transmission disappears and there is practically complete absorption from λ 6760 to λ 6920. The very sharp bands $\lambda\lambda$ 4282, 4300, 4310, 4322 and 4343 do not appear to change very much with change in temperature. On the strip taken at 73° these bands appear sharper than on any of the other strips.

A spectrogram, B, Plate XIX, showing the effect of rise in temperature was made on a 0.17 normal neodymium chloride solution in water 196 mm. deep. The amount of neodymium chloride in the path of the light is approximately the same as in the spectrogram showing the effect of temperature on a 3.4 normal solution in a cell 12 mm. deep. In this case the temperatures were 5°, 16°, 28°, 42°, 59°, 72° and 82°. Exposures were made to the Nernst glower for 3 minutes (current 0.8 ampere and slit width 0.20 mm.). Each strip was exposed to the spark for 6 minutes. The purpose of making this spectrogram was to find the effect of concentration of a salt upon the changes produced by change in temperature.

A description of the bands at 5° and 82° will be given. Any change that takes place between these two temperatures is a gradual one. Transmission begins at λ 2600. Bands appear between $\lambda\lambda$ 3250 and 3300 and $\lambda\lambda$ 3455 and 3575. The band λ 4274 is much sharper and narrower than for the more concentrated solution. The numerous fine bands in the region λ 4300 are very faint. The bands $\lambda\lambda$ 4420 to 4460, $\lambda\lambda$ 4600 to 4630, λ 4645, $\lambda\lambda$ 4680 to 4705, $\lambda\lambda$ 4745 to 4770 and λ 4820 have rather diffuse edges. Wide bands appear from λ 5020 to λ 5290 and from λ 5685 to λ 5920. Diffuse bands are located at λ 5310, λ 6810 and λ 6900. The group in the region λ 6300 appears, but the bands are extremely faint.

At 82° the general absorption has increased in the ultraviolet and has reached to about λ 2800. It will be noticed here that the effect of rise in temperature upon this general ultraviolet absorption is greater for the dilute solution than for the concentrated solution previously described.

The band $\lambda\lambda$ 3455 to 3575 at 5° has widened slightly, having the limits $\lambda\lambda$ 3445 and 3580 at 82°, the widening being about 15 A. U. This band in the concentrated solution widened 60 A. U. Practically no effect on the bands from λ 4200 to λ 4900 is to be noticed with rise in temperature. At the higher temperature the bands are slightly more diffuse, but this change is very small. The band $\lambda\lambda$ 5020 to 5290 at 5° has widened to $\lambda\lambda$ 5015 and 5285, about 10 A. U. The corresponding widening for the concentrated solution was approximately 50 A. U., although it must be noted that in the more concentrated solution this widening was mostly due to the increased absorption of the band λ 5310 at the higher temperatures. The band λ 5685 to λ 5920 at 5° has widened to $\lambda\lambda$ 5775 and 5930, about 20 A. U., compared with a widening of 55 A. U. for the more concentrated solutions. None of the other bands show any appreciable change with change in temperature.

A spectrogram, A, Plate XXII, was made showing the effect of temperature on the absorption spectrum of a 1.66 normal aqueous solution of neodymium bromide, the depth of layer being 6 mm. An exposure of 4 minutes was made

to the Nernst glower (0.8 ampere and a slit width of 0.20 mm.). The length of exposure to the spark was 6 minutes. The temperatures, starting with the strip adjacent to the comparison spark, were 4°, 20°, 36°, 50°, 68° and 83°.

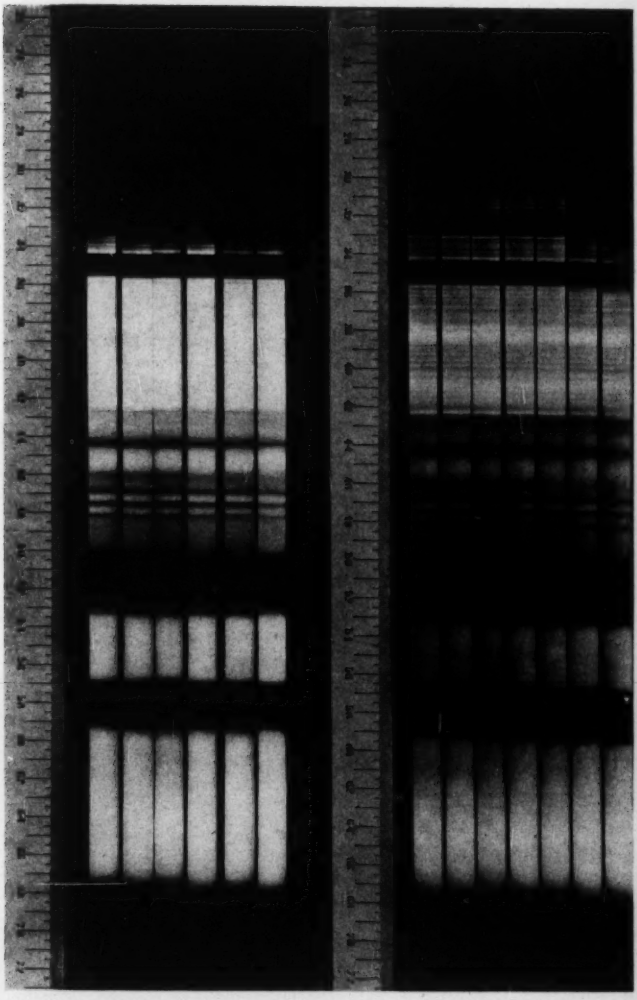
At 4° there is complete absorption in the ultraviolet up to λ 2600. A broad absorption band appears at λ 2660 to λ 2800 and from λ 2950 to λ 3060. These absorption bands appear with a more or less general absorption. Bands appear at $\lambda\lambda$ 3460, 3500 and 3540. The band at λ 4274 is weak. Weak and diffuse bands occur at $\lambda\lambda$ 4440, 4630, 4695, 4760, 4825, 5095, 5260, 6810 and 6900. Wider bands are located at $\lambda\lambda$ 5116 to 5140, $\lambda\lambda$ 5200 to 5240 and $\lambda\lambda$ 5710 to 5850.

At 83° the spectrum is almost exactly the same as at 4°. The ultraviolet absorption is complete up to λ 3050. The bands at λ 3500 have increased in width slightly and the band λ 4274 is slightly broader. The bands that have widened appreciably are $\lambda\lambda$ 5195 to 5260 and $\lambda\lambda$ 5700 to 5880. The change in the absorption is greater when the temperature is changed from 68° to 83°. Up to 68° there is practically no change in the absorption spectrum at all.

A spectrogram, B, Plate XXII, showing the effect of temperature was made, using a 0.055 normal aqueous solution of neodymium bromide, the depth of the layer being 197.4 mm. This spectrogram was made for comparison with that for a 1.66 normal solution of the same salt 6 mm. deep. The exposures to the Nernst glower lasted 90 seconds in this case (current 0.8 ampere and slit width 0.20 mm). The length of exposure to the spark was 6 minutes. Starting with the strip nearest to the comparison scale, the temperatures of the solution were 5°, 16°, 29°, 42°, 55°, 68° and 84°.

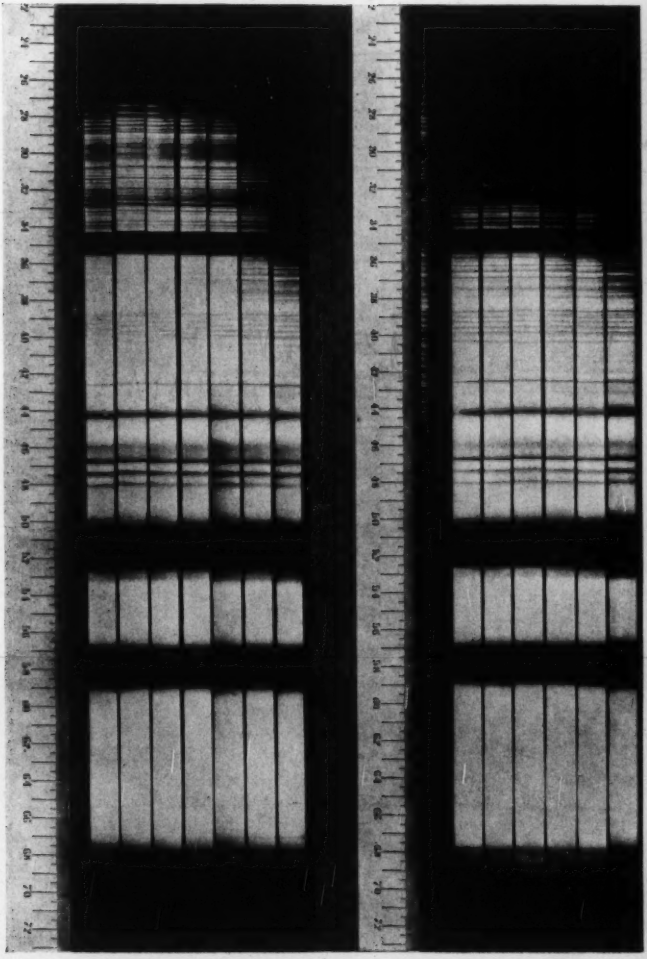
At 5° there is practically complete transmission of light between λ 3400 and λ 2600, no ultraviolet bands appearing, as was the case for the more concentrated solution. The bands $\lambda\lambda$ 4445, 4693, 4760, 4825 and 5095 were somewhat sharper than they were in the concentrated solutions. The two largest bands extended from λ 5200 to λ 5250 and from λ 5710 to λ 5850. As in the case of the more concentrated solution, so here, the greatest change in the absorption took place in

Plate XXI.



B A

Plate XXII.



B A

the change from 68° to 84°. The ultraviolet absorption increased up to λ 2900. The bands at λ 3500 became considerably stronger, but they widened very little. The bands $\lambda\lambda$ 4445, 4693, 4760 and 4825 are somewhat weaker than at 5°. The wide bands remained practically as wide as at 5°, λ 5200 to λ 5250 and λ 5705 to λ 5870. This indicates a widening of about 25 A. U. for the latter band. For the more concentrated solution the widening of these two bands was 25 and 40 A. U., respectively. It is thus seen that in the more concentrated solutions the bands widen more with rise in temperature than they do in the less concentrated solutions. At 42° in the dilute solution there appears a narrow band at λ 6710. This increases in intensity with rise in temperature. This band does not appear at all in the concentrated solution.

A spectrogram, A, Plate XXI, was made of neodymium chloride and calcium chloride in water. Exposures were made for 30 seconds to the Nernst glower, the current being 0.8 ampere and the slit width 0.20 mm. The length of exposure to the spark was 4 minutes. Starting with the strip nearest the numbered scale, the temperatures were 6°, 17°, 31°, 49°, 63°, 74° and 82°.

The general effect of the addition of calcium chloride is to make all the bands hazier, and to increase the transmission throughout the region of the band. At 6° there is a slight transmission throughout the ultraviolet portion of the spectrum. As the temperature is raised this general transmission is decreased, and at 82° practically no light of shorter wave length than λ 2800 passes through the solution. Sharp bands occur at λ 3464, λ 3500, λ 3535, λ 4276 and weak diffuse bands at λ 4295, λ 4305, λ 4340, λ 4445, λ 4620, λ 4695, λ 4760, λ 4825, λ 5095, λ 5130, λ 5225, λ 5260, λ 5320, λ 5710 to λ 5860, λ 6245, λ 6810 and λ 6900.

At 82° the bands in the λ 3500 region are slightly more intense than at 6°. Practically all the bands from λ 4200 to λ 5200 have become much weaker at the higher temperature. This is especially true of the band λ 4276, its intensity being less than half what it is at 6°. Most of the bands are shifted

to the red with reference to the same bands at 6°. For instance, λ 5095 is shifted 5 A. U. towards the red. The bands λ 4695, λ 4760 and λ 4825 are all shifted to the red at the higher temperature, and especially λ 4825, the shift in this case amounting to 5 A. U. In the case of these bands the shift is not an apparent one due to unsymmetrical broadening, for in this instance there is no broadening at all.

The band from λ 5710 to λ 5860 at 6° has widened very unsymmetrically and has the limits λ 5710 to λ 5920. The short wave length side is quite sharp and its position is practically independent of the temperature. The long wave-length edge is quite broad and recedes quite rapidly towards the red as the temperature is raised. The bands in the red, $\lambda\lambda$ 6810 and 6900, grow fainter and fainter with rise in temperature, and have practically disappeared at 82°. The band λ 6245 is very weak at 6° and has disappeared at about 60°.

It will thus be seen that not only does the presence of calcium chloride modify greatly the absorption of neodymium chloride, but that it changes the effects due to temperature very fundamentally. In pure neodymium chloride practically no bands decrease in intensity with rise in temperature, and at present no shift has been detected. When calcium chloride is added to the solution most of the bands decrease in intensity with rise in temperature and several are shifted towards the red at the same time. Several bands disappear. Moreover, although the band $\lambda\lambda$ 6800 to 6900 widens, this widening is entirely on the red side, whereas for the pure neodymium chloride solution this widening always takes place on both sides of the band.

A spectrogram, B, Plate XXI, was made to show the effect of change in temperature upon a 2.15 normal aqueous solution of neodymium nitrate. The length of layer was 3 mm. The exposures were for 40 seconds to the Nernst glower (current 0.8 ampere, slit width 0.20 mm.). The length of exposure to the spark was 6 minutes. Starting with the strip nearest the comparison spark, the temperatures were 4°, 17°, 29°, 43°, 58°, 71° and 84°.

The changes in the spectrum due to this change in temperature of 80° were very slight. The NO_3 band extends to about λ 3250 at 4°, and to about λ 3280 at 84°. The bands at λ 3500 became considerably wider and their edges more diffuse at the higher temperatures. At the lower temperatures fine bands appear at $\lambda\lambda$ 5210, 5225 and 5240. At 84° these bands all merge into a single band. The red band extends from λ 5705 to λ 5860 at 4°. The band at λ 5820 is very faint at the lower temperatures. At 84° it is unrecognizable. At this temperature the red band extends from λ 5700 to λ 5880. The widening of this band for the concentrated solution is somewhat greater than for the dilute solution, but the effect of concentration is very slight. This is to be expected since the effect of temperature itself is so very minute.

A spectrogram, A, Plate XXIII, was made of a 1.66 normal aqueous solution of neodymium bromide 54.6 mm. deep. The exposures were 3 minutes to the Nernst glower and 6 minutes to the spark. The current in the Nernst glower was 0.8 ampere and the slit width 0.20 mm. Starting with the strip nearest the comparison scale, the temperatures were 6°, 20°, 33°, 47°, 62°, 73° and 82°.

The effect of rise in temperature on the absorption spectra of this salt was quite marked, practically all of the bands broadening and becoming more intense. At 6° the ultraviolet absorption extended to λ 3600. At 82° it had advanced to λ 3800. Very narrow and fine bands appear at $\lambda\lambda$ 4186, 4300, 4308, 4345, 6240, 6265, 6290, 6305, and much broader bands at λ 6380 and λ 6740. Wide bands occur from $\lambda\lambda$ 4390 to 4480, $\lambda\lambda$ 4550 to 4850, $\lambda\lambda$ 4990 to 5340, $\lambda\lambda$ 5650 to 5950 and $\lambda\lambda$ 6760 to 6930, at 6°. At 82° these bands have the following limits, respectively: $\lambda\lambda$ 4380 to 4500, $\lambda\lambda$ 4540 to 4910, $\lambda\lambda$ 4960 to 5370, $\lambda\lambda$ 5620 to 5990 and $\lambda\lambda$ 6730 to 6960.

Erbium Chloride. A spectrogram, B, Plate XXIII, was made to show the effect of rise in temperature on the absorption spectrum of a solution of erbium chloride. For this purpose a 0.94 normal solution was used and the depth of layer was 48 mm. The solution probably contained a con-

siderable number of impurities, so that the amount of erbium was in fact quite small. The absorption spectrum was found to change but little with rise in temperature, thus indicating a dilute solution. Exposures were made for 30 seconds to the Nernst glower and 4 minutes to the spark. The current through the glower was 0.8 ampere and the slit width 0.20 mm. Starting with the spectrum nearest the comparison scale, the temperatures were 7°, 17°, 29°, 46°, 60°, 70° and 80°.

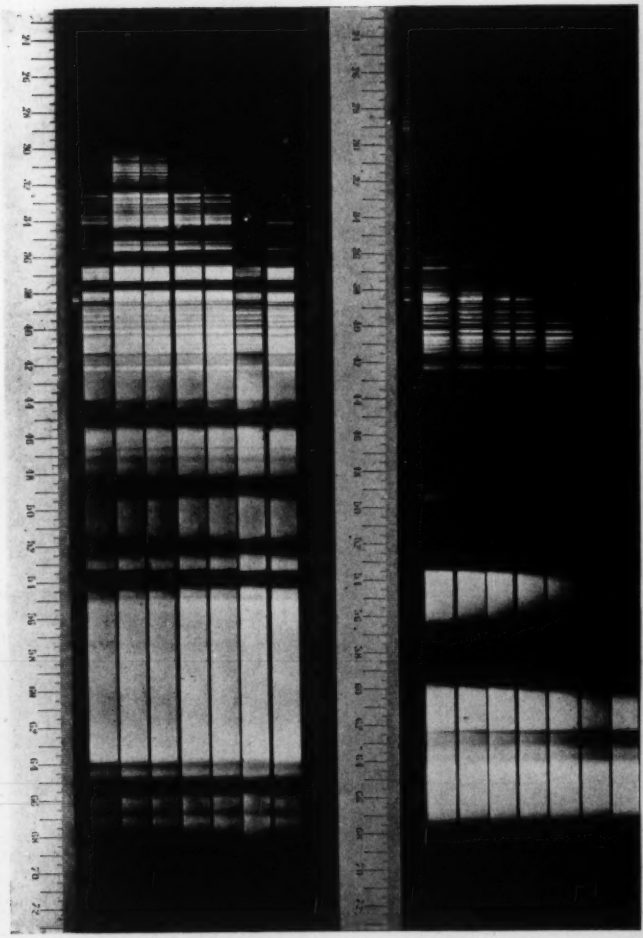
At 70° the ultraviolet is absorbed to λ 3950. As the temperature is raised the ultraviolet absorption increases, and at 80° it reaches λ 3150. Bands from 20 to 40 A. U. wide occur at λ 3235, λ 3510, λ 3640 and λ 3785. These bands are slightly wider at 80°, but as for all the other erbium bands this widening is very small. Weak and narrow bands appear at $\lambda\lambda$ 4165, 4425, 4458, 4500 (strong), 4535, 4540, 4555, 4580, 4685, 4750 (30 A. U. wide), 4810, 4840, 4855, 4870 (strong and 20 A. U. wide), and 4920. λ 4920 lies alongside of a fuzzy band extending from λ 4910 to λ 4950.

After these comes a rather wide band which for a shorter length of layer would most likely be broken up into a number of much finer bands. This band extends from λ 5190 to λ 5250. At λ 5217 a narrow sharp line runs through the fuzzier and wider band. Broad (about 30 A. U. wide) and very faint bands are located at λ 5630 and λ 5760. For greater concentrations these would probably show as finer bands. The band at λ 6540 is much more diffuse on the red than on the violet side, this possibly being due to a component that is not separated at this temperature. Other bands are located at $\lambda\lambda$ 5365, 5380, 5425, 5445, 5505, 6410, 6440, 6495 and 6690.

The general effect of rise in temperature here is to cause the lines to become slightly fuzzier and to show more of a "washed out" appearance. No shift due to rise in temperature was noticed.

Throughout all the previous work the wave lengths were read directly from a scale. This scale was made so as to give the wave lengths in A. U. directly. It was found in the meas-

Plate XXIII.



B A

urements that the Seed films did not correspond to the Wratten and Wainwright films when the same spark spectra on the two kinds of films were placed beside one another. This was probably due to different shrinkage of the two kinds of films on fixing, washing and drying. For this reason the wave length measurements are not absolutely correct but only relatively so. All the temperature work was done with Wratten and Wainwright films. The relative measurements of fine bands for any spectrogram are probably correct to within a few Angström units.

IV. General Results.

In the present spectroscopic investigation our working hypothesis has been that the valency of any atom or radical is due to electrons, and in a compound there are electrons that are outside of the atoms. The charged systems within the atom are supposed to be neutralized so that their electric fields do not extend far from the system. To visualize an atom we must consider that if the whole mass were electromagnetic and the components were electrons, then these electrons would occupy relatively about as much of the space in an atom as the planets do in the solar system. Light waves then would be very large as compared with the atoms, and if the electron systems within the atom are neutralized and the elastic forces large, the absorption of energy would be very small, so that the body will be practically transparent.

It seems quite possible that the second kind of wide absorption bands may be due to the absorption by the valency electrons, or, in the case of the infra red bands, by the ions themselves. The valency electrons and ions will be very greatly modified by the solvent and any foreign salts, such as calcium or aluminium compounds, dissolved in it.

In discussing gas spectra we found that the prevalent belief is that gases radiate and absorb line spectra only when the atoms or molecules are in a peculiar condition. In some cases this condition may be brought about by intense ionization. It is quite probable that when a light wave passes over the UO_2 group or any other group the valency electrons

are set into vibration, and in some cases may even be torn off from the group. This would subject the outer electron systems of the uranium atom to intense electrical forces, and it seems quite possible in this case that the uranium or neodymium atom may be able to absorb or emit a rather fine band spectra. In the case of a gaseous atom or molecule the time between collisions is quite long compared with the frequencies of the light vibrations, and the vibrating electron systems are probably far inside the atom and therefore but slightly affected by neighboring molecules and various physical and chemical changes in the neighborhood. In the case of the vibrating systems of uranium, neodymium and erbium salts, the outside physical and chemical conditions play a very important rôle. Now in the case of a hydrated molecule or ion containing the UO_2 group, it seems that it would be possible to get some knowledge of the forces resulting from an atmosphere if the value of e/m for the various light vibrators were known. In the same way it may be possible to find the effect of the NO_3 group.

Rise in temperature causes the general absorption of any salt in water to increase and also causes the bands to broaden and become more intense.

In general, the increase of the general absorption with rise in temperature is much greater for concentrated solutions. This also holds true for bands of the second type, and to a small extent for bands of the third type.

The presence of calcium and aluminium chlorides causes the chromium chloride bands to widen very unsymmetrically on the long wave-length edge with rise in temperature.

The uranyl chloride bands are shifted towards the red with rise in temperature. No shift for the uranyl nitrate could be noticed. The uranyl acetate and sulphate bands were slightly shifted.

No shift with rise in temperature was noticed for solutions of neodymium or erbium salts. When calcium chloride is present the neodymium chloride bands are, however, shifted, and the remarkable fact is observed that the bands then become fainter with rise in temperature. This latter phenom-

enon is considered to be very important, and it may be that the abnormal Zeeman effect observed by Becquerel is due to the presence of foreign compounds in the tysonite and xenotine crystals.

In concluding, the authors wish to express their thanks to Drs. Pfund and Anderson for many valuable suggestions. They also wish to thank Prof. Ames for the grating and for the ideal conditions under which the work is being done.

PHYSICAL CHEMICAL LABORATORY,
JOHNS HOPKINS UNIVERSITY, October, 1909.

[Contributions from the Chemical Laboratory of Harvard College.]

TETRABROMDIKETOCYCLOPENTENE.

BY C. LORING JACKSON AND H. A. FLINT.

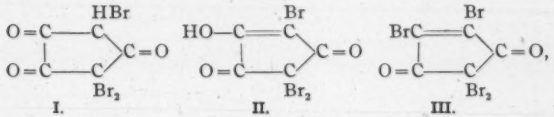
In 1906 F. W. Russe and one of us published[1] a description of a substance prepared by the action of fuming nitric acid and bromine on tetrabrom-*o*-quinone, which had the formula $C_5Br_4O_2$, and was supposed to be a cyclopentene-*o*-quinone. The present paper contains a study of this compound, to which we had hoped to add an account of a white acid containing bromine formed at the same time, but we have not succeeded in finding the conditions under which this acid is formed, obtaining oxalic acid invariably in place of it.

In studying the constitution of the yellow compound melting at 142°, we found that a solution of sodic carbonate decomposed it, giving as the principal product a black tar soluble in water, and in smaller amounts dibrommaleic acid (identified by its melting point, 123°, its properties, and an analysis), and some bromine derivative of methane, which we suppose to be methylene bromide, but the quantity was too small to settle this point with certainty. On these observations we founded a lactone formula, which explained all the observed facts; but, when our work had reached this stage, there appeared a paper by Franz Henle[2] describing a yellow

[1] THIS JOURNAL, **35**, 184 (1906).
[2] Ann. Chem. (Liebig), **352**, 45 (1907).

compound made from the tribromtriketocyclopentane of Hantzsch[1] by the action of phosphoric pentabromide, which, like ours, had the formula $C_5Br_4O_2$, melted at 142°, and agreed with ours in its other properties. To make certain that this compound was identical with ours, some of it was made by Henle's method, and treated with methyl alcohol, when it gave a product, $C_5Br_3OCH_3O_2$, melting at 67°, and with ethyl alcohol a compound, $C_5Br_3OC_2H_5O_2$, melting at 110°; as our compound also gives these derivatives there is no question that these substances are the same.

This identification of our compound with Henle's made it necessary to substitute for our lactone formula that of a cyclopentene, which had been proved to be the correct one, as follows: Hantzsch found that his tribromtriketocyclopentane (made by the action of bromine on a solution of sodic bromanilate) was decomposed by boiling with bromine water into hexabromacetone and oxalic acid. Its constitution therefore must be represented by Formulas I and II,



I. II. III.

I representing the keto, II the enol form. Henle's treatment of this with phosphoric pentabromide replaced the hydroxyl in II by bromine, giving III as the formula for our compound, which is therefore the tetrabromdiketocyclopentene. This formula is in harmony with its conversion into dibrommaleic acid and methylene bromide observed by us, and with all our other observations.

The conversion of tetrabrom-*o*-quinone into the tetrabromdiketocyclopentene offers no difficulties, but as none of the intermediate products have been isolated we do not think it worth while to consider the different series of reactions which may have taken place in this transformation.

Tetrabromdiketocyclopentene is a substance with sharply

[1] Ber. d. chem. Ges., **21**, 2421 (1888).

contrasted properties. On the one hand, it is remarkably stable in presence of acids: for instance, it can be boiled for several hours with fuming nitric acid without visible effect, and bromine, either alone or with water, has no action on it. On the other hand, water, when boiled with it, or ethyl or methyl alcohol, an alkali, or even sodic acetate in the cold decomposes it with great ease. A remarkable instance of this difference in behavior is found in the fact that it can be boiled without action with bromine and water, whereas similar boiling with water alone would produce a small amount of a soluble black decomposition product. It is then, apart from the action of acids, a very reactive substance, and we have prepared from it the following compounds:

With aniline it gives two compounds, one,

$$C_5Br_3(C_6H_5NH)O_2,$$

yellow needles melting at 178°; and a red amorphous body, which does not melt below 300°, and has the composition

$$C_5OH(C_6H_5NH)(C_6H_5N)O_2.$$

Sulphurous dioxide with alcohol and water replaces two atoms of bromine by hydrogen, forming the compound $C_5H_2Br_2O_2$, yellow plates melting at 151°. Phenylhydrazine gives with this dibromdiketocyclopentene a brown amorphous product not melting below 300°, which, on analysis, gave results agreeing with the calculated values for

$$C_5H_2(C_6H_5N_2H_2)_2O(C_6H_5N_2H).$$

Aniline gives with the compound $C_5H_2Br_2O_2$ yellow needles melting at 121°, and having the formula

$$C_5H_2Br(C_6H_5NH)O_2,$$

which are also made by the reduction of tribromanilinodiketocyclopentene (melting point 178°) with sulphurous dioxide. Sodic carbonate in aqueous solution in the cold converts the body $C_5H_2Br(C_6H_5NH)O_2$ into a substance having the composition $C_6H_5NHC_3HO$, yellow needles melting at 221°. Methyl alcohol acts on tetrabromdiketocyclopentene even in the cold, giving the compound $C_5Br_3(OCH_3)O_2$, white needles melt-

ing at 67°. Ethyl alcohol, under the same conditions, gives the ethyl derivative, $C_5Br_3(OC_2H_5)O_2$, white needles melting at 110°. It is noteworthy that in this case the ethyl compound has the higher melting point of the two. Aniline acts on the tribromethoxydiketocyclopentene, giving the compound

$$C_5H_2(OH)(C_6H_5NH)O_2,$$

red and amorphous, melting with decomposition at 140°. The presence of the hydroxyl was confirmed by the formation of the acet compound,

$$C_5H_2(OC_2H_3O)(C_6H_5NH)O_2,$$

amorphous, pale brown, melting at 150° with decomposition.

In determining the positions of the different radicals in the cyclopentene ring we start from the compound

$$C_6H_5NHC_3HO,$$

melting at 221°, made by the action of sodic carbonate on the bromanilinodiketocyclopentene,

$$C_5H_2Br(C_6H_5NH)O_2,$$

melting at 121°. If this compound has the simplest possible molecular weight, containing but one benzene ring, we can find only three possible formulas for it:

I. $(C_6H_5NH)CH = C = CO$;

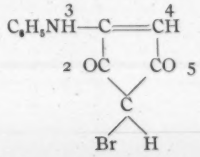
II. $(C_6H_5NH)—CO—C \equiv CH$;

III. $(C_6H_5NH)—C(=CH)—CO$.

I, a ketene, and II, an acetylene, must be exceedingly reactive substances. They must therefore add bromine easily and be promptly attacked by potassic permanganate. Our substance reacts with bromine only after standing over half an hour, and with permanganate the reaction was not complete even after 24 hours; in other respects also it is decidedly sluggish. Formulas I and II, therefore, must be rejected, and III adopted for our substance, which makes it an anilinoketotriene. All its observed properties are such as would

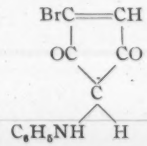
be expected from this formula; thus, it was decidedly stable and was attacked slowly by bromine or potassic permanganate; oxidations gave products without pronounced acid properties; phenylhydrazine reacted with it, and it did not precipitate silver from ammoniacal argentic nitrate. This view of its structure, however, cannot be considered finally established, as it is possible that it may have a larger molecular weight, having been formed by the union of two residues of the cyclopentene to form a ring of more than 3 atoms of carbon—a view which is certainly supported by its high melting point, 221°. Unfortunately, we did not determine its molecular weight, which would have settled the question, so that we can adopt this triene formula only provisionally as one which gives an excellent explanation of the observed facts.

For determining the positions of the radicals in the pentene ring it makes no matter whether the substance is a triene or has a more complex formula, as our argument applies equally well in either case. There are four possible formulas for the bromanilinodiketocyclopentene, from which the triene was formed:

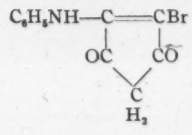


I

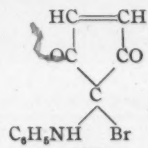
IV.



V.



VI.



VII.

The formation of dibrommaleic acid and methylene bromide, when the compound $C_5Br_4O_2$ is treated with sodic carbonate, makes it probable that if formula V or VII were correct the anilino group would split off attached to one atom of carbon instead of to three, as in our experiment, since in these formulas it is attached to the atom of carbon which was eliminated as methylene bromide from the tetrabrom compound. If, however, either of these substances (V or VII) could form an anilinotriene, it could not have the formula C_6H_5NHCHO found by us, but would contain at least 2 atoms of oxygen. Formulas V and VII must therefore be rejected. The same reasoning applies to VI, which might form a triene, but this would contain two atoms of oxygen, as the atom of bromine would certainly have been replaced by a hydroxyl. Formula VI, therefore, must also be rejected, which leaves Formula IV as the only one possible. That is, the anilino group enters the pentene ring at 3, if we adopt the numbering of the places given with Formula IV.

As the anilino compound, $C_5H_2Br(C_6H_5NH)O_2$, is formed from the dibromdiketocyclopentene, $C_5H_2Br_2O_2$, by replacing one atom of bromine by the anilino group, it follows that this also has the same constitution, $[1,4]H_2[1,3]Br_2$. It certainly would not have been expected that the two atoms of bromine replaced in the reduction would be attached to different parts of the pentene ring, but this is not without analogy, as Hantzsch[1] has observed with chlorpentacarbon rings that only one of the atoms of chlorine in the group CCl_2 is replaced by hydrogen. This view of the structure of the dibrom body is supported by the observations that it gives no methylene bromide when treated with sodic carbonate, and that it is not attacked by alcohol.

The anilino derivative, $C_5Br_3(C_6H_5NH)O_2$, made from the tetrabrom compound, $C_5Br_4O_2$, and melting at 178°, was converted into the monobrom compound,

$$C_5H_2Br(C_6H_5NH)O_2,$$

melting at 121°, on reduction with sulphurous dioxide. The

[1] Ber. d. chem. Ges., **22**, 1238, 2841 (1889).

anilino group must therefore be at 3 in this body; and, as this bromanilino compound, melting at 178°, can be converted by alcohol and aniline into the anilinohydroxydiketocyclopentene, $C_5H_2(OH)(C_6H_5NH)O_2$, melting at 140°, it follows that the anilino radical is at 3 in this compound also. Another way of making this hydroxy derivative was by the action of aniline on the tribromethoxydiketocyclopentene,

$$C_5Br_3(OC_2H_5)O_2,$$

melting at 110°; it follows therefore that the ethoxyl does not enter the ring at the same place as the anilino group. Its position can be made out from the fact that sodic methylate gave dibrommaleic acid with tetrabromdiketocyclopentene, and as it does not seem possible that methyl (or ethyl) alcohol should attack the ring at a different place from sodic methylate, it follows that neither the bromine at 3 nor at 4 could have been replaced, as that would have given brommethoxymaleic acid instead of dibrommaleic acid. This leaves only the constitution $C_5[1,3,4]Br_3[1](OCH_3)$ (or $OC_2H_5)O_2$ for these compounds, and the anilino derivative melting at 140° must be $C_5[1,4]H_2[1]OH[3](C_6H_5NH)O_2$. In the formation of this last substance from the compound $C_5Br_3(OC_2H_5)O_2$ two atoms of bromine have been replaced by hydrogen—a reaction, which it is easy to understand, when aniline is present; and the ethoxyl has been saponified to hydroxyl, which it is harder to explain, but it may have been due to the action of the water in the ether used as a solvent.

The phenylhydrazine derivative of dibromdiketocyclopentene, $C_5H_2Br_2O_2$, would have the structure

$$C_5[1,4]H_2[1,3](C_6H_5N_2H_2)_2[2](C_6H_5N_2H)[5]O.$$

The action of the phenylhydrazine on one of the keto groups only is in harmony with the observations of Hantzsch and Zincke with other diketopentacarbon rings. The composition of this substance furnishes a partial confirmation of the constitution $C_5[1,4]H_2Br_2O_2$, assigned to dibromdiketocyclopentane, for, if the two atoms of bromine had stood at 1,1, only two phenylhydrazine residues would have entered the

molecule; the presence of 3 therefore excludes one of the 3 possible formulas; but in considering this argument and the structure worked out for this compound it must be remembered that it is amorphous and melts above 300°, which may indicate a more complex formula than the one adopted by us. The same doubt applies to the only substance still unconsidered, the compound $C_5OH(C_6H_5NH)(C_6H_5N)O_2$, as it is also amorphous, and does not melt below 300°. Although the formula given agrees best with the analyses, it is not established with certainty, since the formula

$$C_5H(OH)(C_6H_5NH)_2O_2$$

gives percentages not very far removed from those obtained experimentally, and one cannot have much confidence in a purification effected by washing only. Under these conditions we think it not worth while to discuss the constitution of this body.

EXPERIMENTAL PART.

Preparation of Tetrabromdiketocyclopentene, $C_5Br_4O_2$.—Twenty grams of tetrabrompyrocatechin (or tetrabrom-*o*-quinone) were mixed with 100 cc. of fuming nitric acid and 10 cc. of bromine, and the mixture heated on the steam bath in a flask until all the bromine had been given off, which usually took 30–40 minutes. The hot solution was then diluted with about 250 cc. of water, which threw down the product, either as a finely divided precipitate or as a reddish brown oil; in either case it was heated with the dilute nitric acid on the steam bath with constant stirring until it was converted into large yellow crystals. These were filtered out, washed thoroughly with water, and recrystallized from a mixture of equal parts of benzene and ligroin, until they showed the constant melting point 142°.

The method described above is essentially that by which the substance was first prepared by Russe and one of us.[1] In that work, however, the yellow product was accompanied by a white acid containing bromine. We at first tried to prepare this white acid by evaporating the aqueous mother

[1] This Journal, **35**, 184 (1905).

liquors, from which the yellow crystals had been deposited, but the product was nothing but oxalic acid containing a trace of these crystals. As the acid containing bromine might have been oxidized to oxalic acid by the evaporation with nitric acid, an attempt was next made to obtain it by shaking out the mother liquors with ether, but here also the extract, of which there was very little, proved to be nothing but oxalic acid. That the substance was oxalic acid was shown by its calcium, ammonium and aniline salts. The last melted at 170°–180°, and by melting was converted into oxanilide melting at 242°. In spite of many experiments we have not succeeded in reproducing the conditions under which Russe's white acid was formed. That this was not oxalic acid was proved by its melting point, 144°–146°, and by a number of analyses made by Dr. Russe, which gave large percentages of bromine, but, as the substance used evidently was not fully purified, it is not worth while to publish them.

Composition of the Tetrabromdiketocyclopentene.—In order to collect in this paper all the data in reference to this subject, we repeat the analyses and properties[1] already published by Russe and one of us:

	Calculated for $C_5Br_4O_2$.	Found. I.	II.	III.	IV.
C	14.57	15.17	14.43	....	....
H	0.00	0.35	0.19	....	....
Br	77.67	....	....	77.67	77.69

" *Properties.*—It crystallizes from fuming nitric acid in thick plates, from a mixture of benzene and ligroin in large prisms, which are apparently monoclinic. Its color is a full yellow like that of potassic chromate. It melts at 142° with no signs of decomposition, and is soluble in alcohol, ether, chloroform, benzene, or acetone; slightly soluble in ligroin; insoluble in water."

Various Reactions of Tetrabromdiketocyclopentene.—This substance was very little affected by cold water even when shaken with it for a week, but, if boiled with water, it was decomposed, forming in a few hours a very dark solution which

[1] THIS JOURNAL, **35**, 185 (1905).

gave a test for hydrobromic acid. An aqueous solution of sodic acetate acted on it even in the cold, forming a dark-colored solution, which, after acidification, gave on extraction with ether a viscous product. With an aqueous solution of sodic carbonate a similar result was obtained, which will be described in detail later in this paper. The hydrochloride of hydroxylamine reacted with it, when the mixture was warmed on the steam bath, but no definite product could be isolated. The substance also reacted with methyl or ethyl alcohol in the cold, forming compounds which will be described in a later paragraph.

The action of zinc and dilute sulphuric acid or of a warm aqueous solution of stannous bromide seemed to produce a far-reaching decomposition, which may have been due to the action of the water, while sulphurous dioxide with alcohol and water brought about the replacement of two atoms of bromine by two of hydrogen. The action of aluminum amalgam and alcohol for an hour on the steam bath gave no reduction, the product being the ethoxy compound; and sodium in dry ether had no action whatever.

On the other hand, this substance, which is so sensitive toward water, alcohols or alkalies, shows a marked stability toward some other classes of reagents. Bromine, for instance, has no action on it, as was shown by dissolving some of the substance in glacial acetic acid, adding two drops of bromine, and allowing the solution to stand overnight at ordinary temperatures. In the morning the color of the solution was essentially unchanged, and the original compound was recovered from it unaltered. A similar result was obtained when chloroform, carbonic tetrachloride or carbonic disulphide was used as the solvent instead of glacial acetic acid. In fact the presence of bromine prevented the action of water on it, for one gram of the substance, after being warmed with bromine and water for four hours, was recovered unchanged, whereas water alone would have caused a considerable decomposition under these conditions. This resistance to acid oxidizing agents was also shown by boiling it for four hours with fuming nitric acid with no effect. A neutral solution of

potassic permanganate decomposed it, to be sure, but this, was undoubtedly on account of the water and the alkali formed in the reaction. It was also unaffected by acids, such as strong sulphuric acid, whether hot or cold, or diluted with water, or with water and alcohol, or dilute nitric acid, or a solution of hydrobromic acid, even when heated with it for several hours on the steam bath. Glacial acetic acid too produced no effect on it, and the same was true of acetic anhydride, acetyl chloride, or benzoyl chloride. We have then a substance showing a really extraordinary resistance toward acids or oxidizing agents, but attacked with such ease by water, alcohols or alkaline solutions that this property forms a serious obstacle in the way of studying the action of various reagents upon it.

Action of Sodic Carbonate in Aqueous Solution on Tetrabromdiketocyclopentene.—Ten grams of the substance were mixed with 20 grams of sodic carbonate dissolved in 150 cc. of water and the mixture allowed to stand in a corked Erlenmeyer flask at ordinary temperatures for several days, with occasional shaking. The aqueous liquid soon turned dark, and, as the solid disappeared, the color deepened, until it was black and nearly opaque. The product was worked up after the substance had dissolved, which happened in less than a week. As the liquid smelt of some bromine derivative of methane, it was extracted with ether, which, on careful evaporation, left a small amount of a dark liquid with an odor like that of bromoform, but it appeared in such small quantities that in order to obtain enough to purify for analysis and a determination of the boiling point, it would have been necessary to devote to the experiment an outlay of time and labor out of all proportion to the value of the result. All our experiments on this body, including the formation of phenyl isocyanide, seemed to indicate that it was bromoform, but, as no explanation can be found for the formation of bromoform under these conditions from the tetrabromdiketocyclopentene, we are inclined to think, in the absence of convincing experiments, that it was methylene bromide, which would be the natural product of the decomposition.

The alkaline aqueous liquid, after the extraction with ether, was acidified with sulphuric acid, and, as no precipitate was formed, again extracted with ether several times, which removed from it a black, sticky, tarry mass easily soluble in ether, water, or alcohol, but nearly insoluble in the other common solvents. The preparation of a definite compound from this product gave much trouble, but after several experiments we finally succeeded by using the following method: The tarry mass, after it had stood for several weeks until it had partially solidified, was treated repeatedly with toluene, to which a few drops of alcohol had been added. The solutions thus formed, when poured off and evaporated to dryness, gave solid residues, which in different experiments varied from brown to nearly white; they were purified by many recrystallizations from toluene with a few drops of alcohol, until they became pure white and showed the constant melting point 123°, when the substance was dried *in vacuo* for analysis.

The yield at best would have been small, as in the process two of the four atoms of bromine were removed, but it was still more diminished by the formation of the black tar, which was the principal product of the action, the amount of the white substance being so minute that many preparations were necessary to obtain enough of it for analysis. As, too, its purification was very laborious, this work occupied not far from a year.

I. 0.1157 gram of the white acid gave 0.1583 gram AgBr.
II. 0.1654 gram substance gave 0.2266 gram AgBr.

	Calculated for $C_4Br_2O_4H_2$.	Found. I.	II.
Br	58.38	58.24	58.30

These analyses agree therefore with the calculated values for dibrommaleic acid, and that the substance is this acid is proved by the melting point, 123° (Ciamician and Silber[1] give 123°.3), and the other properties, which were as follows: White needles easily soluble in water, alcohol, methyl alcohol, ether, or acetone; nearly insoluble in the other common

[1] Ber. d. chem. Ges., **17**, 558 (1884).

solvents. Strong hydrochloric acid has no visible effect on it; strong nitric acid, when warm, converts it into oxalic acid, hydrobromic acid, and carbonic dioxide; strong sulphuric acid dissolves it. The calcium and barium salts are white and soluble, the lead and silver salts white precipitates; the latter explodes on heating.

The black liquid formed by the action of sodic carbonate on tetrabromdiketocyclopentene contained a larger amount of sodic bromide than would correspond to the formation of dibrommaleic acid. This was not unexpected, however, as much of this acid might have suffered a further decomposition, and also a larger amount of the bromide might have been formed in the reaction leading to the black tar, which was the principal product of this reaction. This tar was soluble in water, ethyl or methyl alcohol, or ether, and apparently a large part of it was left in the aqueous liquid, after it had been extracted thoroughly with ether. Although we have devoted a great deal of time and work to this substance, we have not succeeded in extracting from it any definite compound except the dibrommaleic acid.

Action of Sodic Methylate on Tetrabromdiketocyclopentene.—Five grams of the substance mixed with a methyl alcohol solution of an excess of sodic methylate were allowed to stand several days at ordinary temperatures, until all the solid had disappeared. The very dark solution was then saturated with carbonic dioxide and the precipitated salts filtered out. As the filtrate gave no appreciable amount of organic residue after evaporation, the product of the reaction was sought in the precipitate by dissolving it in dilute nitric acid and extracting several times with ether, which, on evaporation, left a dark tarry mass. By treating this with toluene and a few drops of alcohol, and purifying by recrystallization from the same mixture of solvents, dibrommaleic acid was isolated and recognized by its melting point, 123°, its solubility in the organic solvents, and the solubilities of its calcium, barium, lead and silver salts. Sodic methylate, in a solution of methyl alcohol, therefore acts on tetrabromdiketocyclopentene in the same way as an aqueous solution of sodic carbon-

ate. Sodic ethylate gave a black, sticky mass, similar to that obtained with the methylate. It was not thought worth while to study it further.

Action of Aniline on Tetrabromdiketocyclopentene.

I. Tribromanilinodiketocyclopentene, $C_5Br_3(C_6H_5NH)O_2$.—Ten grams of tetrabromdiketocyclopentene and 10 cc. of aniline were dissolved in 300 cc. of ether, when a precipitate of hydrobromide of aniline was thrown down immediately. The mixture was allowed to stand a few minutes with occasional shaking, until no further precipitate was formed, after which it was filtered and the filtrate evaporated to about one-half its volume, when, upon adding a large excess of ligroin, a brown precipitate was obtained, and this was filtered out and recrystallized from a mixture of equal parts of benzene and ligroin, until it showed the constant melting point 178°, when it was dried *in vacuo* for analysis.

I. 0.2027 gram substance gave 0.2684 gram AgBr.

II. 0.2214 gram substance gave 0.2941 gram AgBr.

	Calculated for $C_5Br_3C_6H_5NHO_2$.	Found. I.	II.
Br	56.60	56.35	56.53

Properties of Tribromanilinodiketocyclopentene.—Yellow needles, which melt at 178° without decomposition. Easily soluble in alcohol, methyl alcohol, ether, chloroform, or acetone; moderately soluble in benzene, toluene, or glacial acetic acid; insoluble in cold ligroin, more soluble when it is hot. Strong hydrochloric acid has no effect on it, whether hot or cold; strong nitric acid gives a yellow solution, from which water precipitates nothing; strong sulphuric acid gives an orange solution, from which water apparently precipitates the original substance. Aqueous sodic hydrate gives a yellow solution with it, having the characteristic odor of phenyl isocyanide. A solution of sodic carbonate formed a brown solution, from which, after acidification, a dark oil can be extracted with ether. An excess of aniline, warmed with an alcoholic solution of the substance, forms a red amorphous product, described in the next section.

The behavior of tribromanilinodiketocyclopentene with the following reagents was also studied. Water warmed with it on the steam bath for three hours attacked it slightly, forming a brown solution, which, on evaporation, yielded only a little tar and hydrobromide of aniline. Alcohol had no effect on it after standing at ordinary temperatures for 2 days, or boiling for 3 hours. Acetic anhydride had no action on it even after standing overnight. Phenylhydrazine was mixed with a solution of it in chloroform and alcohol; the mixture was warmed on the steam bath and then allowed to stand at ordinary temperatures for a day; the product was a brown mass decomposing at 135°–140°, from which we did not succeed in isolating any substance fit for analysis. Two grams of the aniline compound were dissolved in glacial acetic acid, a few drops of bromine added, and the mixture allowed to stand for 3 days. On diluting with water two different substances were obtained, one of which was yellow and melted at about 138°, the other nearly white and melted at about 145°, but as we thought it probable that part of the bromine had entered the phenyl group, we did not think it worth while to take the time to study them.

II. Hydroxyanilinoanildiketocyclopentene, $C_5OH(C_6H_5NH)(C_6H_5N)O_2$.—This substance was formed instead of the monoanilino compound just described, when tetrabromdiketocyclopentene was heated with aniline and alcohol as follows: Five grams dissolved in 95 per cent. alcohol and mixed with 10 cc. of aniline were warmed for half an hour on the steam bath, when, on cooling, the dark reddish-brown liquid deposited a dark red product, which was filtered out. All attempts to purify this substance by recrystallization failed, since the only liquid which dissolved it freely enough was aniline, and from this no good crystals could be obtained; it was therefore washed with alcohol, water, alcohol again, and ether, after which it was dried *in vacuo* for analysis:

I. 0.1782 gram substance gave 0.4643 gram CO_2 and 0.0730 gram H_2O.

II. 0.1687 gram substance gave 0.4351 gram CO_2 and 0.0584 gram H_2O.

III. 0.1988 gram substance gave 17.9 cc. N_2 at 29° and 753 mm.

IV. 0.2394 gram substance gave 21.3 cc. N_2 at 22°.7 and 757.1 mm.

	Calculated for $C_5OHC_6H_5NHC_6H_5NO_2$.	Found. I.	II.	III	IV.
C	69.89	71.06	70.34	....	....
H	4.11	4.55	3.85	....	....
N	9.59	....	....	9.73	10.01

These analyses agree as nearly as could be expected from a substance which could be purified only by washing. The formula calculated from them would indicate that one of the atoms of bromine in the tetrabromdiketocyclopentene had been replaced by hydroxyl. There is a strong analogy for such a replacement in the action of aniline on the ethoxy compound, $C_5Br_3OC_2H_5O_2$, which, as described later in this paper, forms a body having the composition

$$C_5H_2OH(C_6H_5NH)O_2,$$

and, as this is also formed by the action of aniline and alcohol on tribromanilinodiketocyclopentene,

$$C_5Br_3(C_6H_5NH)O_2,$$

it is evident that the hydroxy group can be introduced easily under these conditions. As the tribromanilino compound,

$$C_5Br_3(C_6H_5NH)O_2,$$

must be the first product of the action of aniline and alcohol on tetrabromdiketocyclopentene, it follows that they can convert this body either into the compound

$$C_5OH(C_6H_5NH)(C_6H_5N)O_2$$

or

$$C_5H_2OH(C_6H_5NH)O_2,$$

according to the conditions under which they act.

Properties. It is a dark red amorphous powder which does not melt below 300° and is slightly soluble in hot alcohol, methyl alcohol, chloroform, benzene, toluene, or glacial acetic acid; insoluble in hot ether, or ligroin; very soluble in aniline,

but no good crystals could be obtained from this solution. Strong hydrochloric acid has no visible effect on it; strong nitric acid, or strong sulphuric acid, dissolves it. Sodic hydrate has no action on it at first, but after warming on the steam bath for several days it was found that part of the red solid had disappeared and there was a slight odor of phenyl isocyanide. Upon acidifying the solution with hydrochloric acid and extracting with ether only a little tar was obtained, and this looked so unpromising that it was not studied.

A substance with properties similar to those of the compound $C_5OH(C_6H_5NH)(C_6H_5N)O_2$ was formed by the longer action of aniline on the monoanilino body, $C_5Br_3(C_6H_5NH)O_2$, as a specimen of this compound, which had stood 4 days with aniline and ether, gave, after the aniline had been removed with hydrochloric acid and water, a brown residue, from which none of the monoanilino body could be extracted. It did not melt below 300°, was essentially insoluble in all the organic solvents, and contained no bromine, but to judge from its method of formation probably did not contain hydroxyl.

Reduction of Tetrabromdiketocyclopentene.

Dibromdiketocyclopentene, $C_5H_2Br_2O$.—The best method of obtaining this substance consisted in saturating with sulphurous anhydride a solution of several grams of tetrabromdiketocyclopentene in a mixture of three parts of water to one of alcohol and shaking the mixture for 10 to 12 hours. The solution was then filtered and the filtrate allowed to evaporate spontaneously, after which the slightly colored feathery crystals obtained were purified by crystallization from a mixture of equal parts of benzene and ligroin until they showed the constant melting point 151°, when they were dried *in vacuo* for analysis.

If a shaking machine is not available, the mixture can be allowed to stand overnight, but the product is less pure and abundant in this case. The liquid, after the reaction had taken place, gave a strong test for hydrobromic acid. The success of the process depended on using the proper proportions of water and alcohol. If more than one part of alcohol

to three of water was used the liquid took on a red color and the resulting crystals were also red, and in this case it was almost impossible to purify them. Even with 25 per cent. alcohol some of this red impurity was formed, but this was removed by the crystallization. We are unable to give any explanation of this color. If, on the other hand, the amount of alcohol was diminished, the reaction ran very slowly, so that standing for several days was necessary to get the result with a solution containing only 5 per cent. of alcohol, but, on the other hand, the product was free from color. Using the solutions hot, substituting methyl for ethyl alcohol, or passing the sulphurous dioxide into a moist benzene solution gave no better results.

I. 0.3255 gram substance gave 0.2762 gram CO_2 and 0.0280 gram H_2O.

II. 0.1268 gram substance gave, by the method of Carius, 0.1886 gram AgBr.

III. 0.1358 gram substance gave 0.1996 gram AgBr.

IV. 0.1453 gram substance gave 0.2149 gram AgBr.

	Calculated for $C_5H_2Br_2O_2$.	Found.			
		I.	II.	III.	IV.
C	23.62	23.14	....	....	....
H	0.79	0.96	....	....	....
Br	62.99	....	63.30	62.55	62.94

Properties of Dibromdiketocyclopentene.—It crystallizes in slightly yellow plates, which seem to belong to the orthorhombic system. It melts at 151° without decomposition and is easily soluble in ethyl or methyl alcohol or ether, but when such a solution is warmed for several hours, or allowed to stand in the cold for some days, decomposition sets in, as shown by the appearance of a dark color; soluble without decomposition, even when heated, in chloroform, benzene, toluene, or glacial acetic acid; slightly soluble in hot ligroin, but essentially insoluble in cold. The best solvent for it is a mixture of equal parts of benzene and ligroin. Strong hydrochloric acid has no effect on it; strong nitric acid, or sulphuric acid, dissolves it, when hot, apparently without decomposition, but dilute nitric acid on the steam bath gives oxalic

and hydrobromic acids; alkalies, including ammonic hydroxide, decompose it, forming a dark brown solution. Two grams of it were allowed to stand with sodic carbonate in aqueous solution for several days with occasional shaking, when a black solution was formed like that obtained from tetrabromdiketocyclopentene, but no odor of any bromine derivative of methane was observed. The black solution was not studied.

Two grams of the dibromdiketocyclopentene were dissolved in glacial acetic acid or chloroform and a few drops of bromine added. The color of the bromine soon disappeared, and more was added in small portions as the color vanished, until an excess was present. Upon adding a quantity of water a precipitate was thrown down, which was proved by its melting point, 142°, and appearance to be the tetrabromdiketocyclopentene, $C_5Br_4O_2$.

Acetic anhydride left dibromdiketocyclopentene unaltered after standing overnight with it; but argentic acetate in alcohol in the cold gave a dark solution with a brown precipitate so finely divided that it could not be filtered out, but no argentic bromide. With dilute nitric acid in the cold the dibrompentene was converted in carbonic dioxide, oxalic acid and hydrobromic acid, or bromine. Potassic permanganate with sulphuric acid behaved in a similar way.

Action of Phenylhydrazine on Dibromdiketocyclopentene.— Ten cc. of phenylhydrazine were added to 2 grams of the substance dissolved in benzene, and the mixture, after warming on the steam bath, was allowed to stand overnight at ordinary temperatures. The brown amorphous body, which had separated, was washed with benzene, alcohol, a mixture of water and alcohol and ether, after which it was dried *in vacuo* for analysis:

I. 0.2064 gram substance gave 0.5224 gram CO_2 and 0.0803 gram H_2O.

II. 0.0867 gram substance gave 0.2210 gram CO_2 and 0.0458 gram H_2O.

III. 0.1428 gram substance gave 27 cc. N_2 at 23°.5 and 755.5 mm.

IV. 0.1467 gram substance gave 26.2 cc. N_2 at 16°.4 and 764 mm.

	Calculated for $C_5H_2(C_6H_5NHNH)_2(C_6H_5NHN)O$.	Found. I.	II.	III.	IV.
C	69.35	68.90	69.52	....	....
H	5.53	4.35	5.91	....	....
N	21.10	....	....	21.12	20.90

The analyses agree as well as could be expected from a substance which could be purified only by washing, and indicate that the substance was formed by replacing both the bromine atoms and one of the atoms of oxygen by phenylhydrazine groups, but the substance is so indefinite that its composition cannot be considered finally established. It is a brown amorphous powder which does not melt below 300°, is essentially insoluble in all the common solvents, but decomposed by both acids and alkalies.

Action of Aniline on Dibromdiketocyclopentene.

Bromanilinodiketocyclopentene, $C_5H_2Br(C_6H_5NH)O_2$.—When 7 grams of the reduced body were dissolved in ether, and 10 cc. of aniline added, hydrobromide of aniline appeared almost at once, but after standing at ordinary temperatures for several minutes with occasional shaking the precipitate ceased to form, and then it was filtered out and hydrobromic acid gas passed into the liquid until all the aniline was removed. The salt was filtered out and the filtrate, on evaporation to dryness, left a dark residue, which was extracted several times with a mixture of equal parts of benzene and ligroin. The yellow crystalline extract was purified by recrystallization from the same mixture until it showed the constant melting point 121°, when it was dried *in vacuo* for analysis—I.

The substance was also prepared by the reduction of tribromanilinodiketocyclopentene, $C_5Br_3(C_6H_5NH)O_2$, by shaking this compound for 10 to 12 hours with 25 per cent. alcohol saturated with sulphurous dioxide, after which the liquid was filtered and allowed to stand till all the sulphurous dioxide had escaped, when from the spontaneous evaporation yellow crystals shaped like feathers were deposited. These, after crystallization from a mixture of equal parts of benzene and

ligroin, showed the constant melting point 121°—Analysis II. It is noteworthy that no red color appeared during this reduction, even when fairly strong alcohol was used. In this respect it differed markedly from the reduction of the tetrabrom body.

I. 0.1024 gram substance gave 0.0726 gram AgBr.

II. 0.1234 gram substance gave 0.0872 gram AgBr.

	Calculated for $C_5H_2Br(C_6H_5NH)O_2$.	Found. I.	Found. II.
Br	30.07	30.17	30.07

Properties of Bromanilinodiketocyclopentene.—Fine yellow needles melting at 121° with decomposition. Easily soluble in alcohol, methyl alcohol, ether, chloroform, acetone, benzene, toluene, or glacial acetic acid; almost insoluble in cold ligroin, more soluble in hot. Strong hydrochloric acid has little effect on it; strong nitric acid or sulphuric acid forms a yellow solution, with which water gives no precipitate. Dilute nitric acid does not attack it, even when warmed on the steam bath, but if it is allowed to stand in the cold with strong nitric acid for several weeks, it is decomposed into hydrobromic and oxalic acids. Warm potassic permanganate solution produces the same effect except that the oxalic acid is burnt to carbonic dioxide. A 30 per cent. solution of hydric dioxide had no action on it even after standing for several days. Sodic hydrate dissolves it with a slight odor of phenyl isocyanide and forms a dark solution. Sodic carbonate converts it into a yellow crystalline compound described later.

A chloroform solution of the compound $C_5H_2Br(C_6H_5NH)O_2$ gave with bromine a product with the constant melting point 153°, but our analyses have not led to any probable formula, so that we are of the opinion that it is a mixture of compounds containing different amounts of bromine.

If in preparing the anilino derivative the aniline was allowed to act on the dibromdiketocyclopentene overnight instead of a few minutes, the ethereal filtrate from the hydrobromide of aniline left, on evaporation, a reddish brown amorphous substance undoubtedly analogous to that obtained by the more decided action of aniline on the tetrabrom compound.

As it was of little interest, we did not attempt its purification, which, owing to its indefinite properties, promised to be a difficult task.

Action of Sodic Carbonate on Bromanilinodiketocyclopentene.

Anilinoketotriene, $C_6H_5NHC_3HO$.—Two grams of the bromanilino body (melting at 121°) were mixed with a cold saturated solution of sodic carbonate and allowed to stand for about one week. The substance gradually dissolved, forming a brown solution and giving a faint smell of phenyl isocyanide. As time went on this solution deposited a mass of very fine yellow crystals, which were filtered out, washed thoroughly with water, and crystallized from benzene until they showed the constant melting point 221°, when they were dried *in vacuo* for analysis:

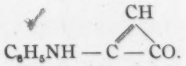
I. 0.2051 gram substance gave 0.5588 gram CO_2 and 0.0931 gram H_2O.

II. 0.2909 gram substance gave 26.01 cc. N_2 at 25° and 750.4 mm.

III. 0.1955 gram substance gave 17.10 cc. N_2 at 22° and 764.6 mm.

	Calculated for $C_6H_5NHC_3HO$.	Found. I.	II.	III.
C	74.48	74.31	....	....
H	4.83	5.07	....	....
N	9.65	....	9.84	9.98

As has been shown in the introduction, this substance is in all probability the anilinoketotriene,



$C_6H_5NH-C(=CH)-CO$.

Properties of Anilinoketotriene.—It crystallizes in good-sized yellow needles, which melt sharply at 221° with decomposition. It is easily soluble in ethyl or methyl alcohol, ether, chloroform, acetone, ethyl acetate, benzene, toluene, or glacial acetic acid; essentially insoluble in ligroin or water. Solutions of the strong alkalies have no effect on it in the cold, and decompose it only slowly when warmed on the

steam bath. Strong hydrochloric acid has no visible effect upon it; strong sulphuric acid gives a purple solution with it; strong nitric acid also dissolves it with a purple color, and when warmed on the steam bath decomposes it, but the product was not studied, except to show that no oxalic acid is formed. Dilute nitric acid, under the same conditions, decomposes it with an odor of nitrobenzene. Upon extracting the liquid product with ether almost white crystals were obtained, which melted between 95° and 100° and showed no acid properties, as they did not change litmus paper or decompose carbonates. We did not have enough of this product for study. Potassic permanganate in dilute solution gave at the end of one hour an odor of phenyl isocyanide with, however, only a slight change of color; even after 24 hours the solution was not colorless, but at the end of 48 hours the color of the permanganate had disappeared entirely. The organic product was not studied. With a 30 per cent. solution of hydric dioxide a white compound was formed after several days, which was only slightly soluble in ammonic hydrate. The triene did not give metallic silver with an ammoniacal solution of argentic nitrate.

If dissolved in chloroform and mixed with a small quantity of bromine, no addition of the bromine could be observed in the first half hour; after this, however, a reaction took place, but, as part of the bromine at least undoubtedly entered the anilino group, it was hardly worth while to study the product. Phenylhydrazine gave a brown, rather tarry product, melting with decomposition at 110°, which came down in an amorphous state from all its solutions.

Action of Methyl Alcohol on Tetrabromdiketocyclopentene.

Tribrommethoxydiketocyclopentene, $C_5Br_3OCH_3O_2$.—Two grams of the tetrabromdiketocyclopentene dissolved in methyl alcohol were allowed to stand at ordinary temperatures for 4 days. At the end of this time the liquid, which gave a strong test for hydrobromic acid, was diluted with water, when a mass of very fine, nearly white, crystals was precipitated. This was filtered out and purified by crystallization from dilute

methyl alcohol until the white crystals showed the constant melting point 67°, when they were dried *in vacuo*:

I. 0.3720 gram substance gave 0.2777 gram CO_2 and 0.0325 gram H_2O.

II. 0.1368 gram substance gave 0.2141 gram AgBr.

	Calculated for $C_5Br_3OCH_3O_2$.	Found. I.	II.
C	19.83	20.36	....
H	0.82	0.98	....
Br	66.11	....	66.60

Properties of Tribrommethoxydiketocyclopentene.—It crystallizes in fine white needles melting to a colorless liquid at 67°. It is easily soluble in ethyl or methyl alcohol, ether, chloroform, acetone, benzene, or toluene; slightly soluble in hot ligroin, but essentially insoluble in cold. To judge from the appearance of a red color all these solutions show a tendency to decompose when heated, as for instance, when they are evaporated on the steam bath. Strong hydrochloric acid has no visible effect on it, but it dissolves apparently without change in strong nitric acid, or sulphuric acid. Alkalies decompose it, giving a dark-colored solution, and what seems to be a similar decomposition is brought about even by boiling it with water.

A solution of sodic carbonate in the cold slowly formed a dark solution, but this reaction was accompanied with no smell of a substituted methane. No action was observed, when a solution of the compound $C_5Br_3OCH_3O_2$ in glacial acetic acid was allowed to stand with bromine. Sulphurous dioxide with methyl alcohol and water acted upon it, giving a red solution, but the product was so tarry that we did not undertake its investigation. When an ethereal solution was mixed with aniline a red product was formed, probably identical with that obtained from the ethoxy body.

Action of Ethyl Alcohol on Tetrabromdiketocyclopentene.

Tribromethoxydiketocyclopentene, $C_5Br_3OC_2H_5O_2$.—Five grams of the tetrabromdiketocyclopentene were dissolved in 100 cc. of 95 per cent. alcohol by warming on the steam bath for a

few minutes, and the solution was allowed to stand overnight at ordinary temperatures. A large excess of water was then added and the nearly white crystalline precipitate recrystallized from a mixture of alcohol and water until it showed the constant melting point 110°, when it was dried *in vacuo* for analysis:

I. 0.1902 gram substance gave 0.2842 gram AgBr.
II. 0.1986 gram substance gave 0.2966 gram AgBr.

	Calculated for $C_5Br_3OC_2H_3O_2$.	Found. I.	II.
Br	63.66	63.59	63.55

Properties of the Tribromethoxydiketocyclopentene.—Small, white needles which melt at 110° without decomposition. Easily soluble in alcohol, methyl alcohol, ether, chloroform, acetone, benzene, toluene, or glacial acetic acid; slightly soluble in ligroin when cold, more soluble when hot; insoluble in water. The best solvent for it is a mixture of alcohol and water. Strong hydrochloric acid has no visible effect on it; strong nitric acid dissolves it slightly; strong sulphuric acid dissolves it, and it is precipitated apparently unchanged by the addition of water. Aqueous sodic hydrate forms a dark solution, which does not smell of a bromine derivative of methane. A similar dark solution was obtained by heating an alcoholic solution of the ethoxy body with sodic acetate, or potassic cyanide, for 3 hours on the steam bath, but only amorphous organic products resulted. Argentic acetate also decomposed the alcoholic solution in the cold, forming argentic bromide and a brown oily product, from which no definite compound could be isolated. Plumbic nitrate and a solution in 50 per cent. alcohol on the steam bath behaved in a similar way, giving much plumbic bromide, but in this case no organic product could be found.

Action of Aniline on Tribromethoxydiketocyclopentene.—Two grams of the ethoxy compound were dissolved in ether and mixed with 2.2 cc. of aniline. After the mixture had stood a few minutes with occasional shaking, no more hydrobromide of aniline was precipitated. The solution was then filtered, evaporated to dryness, and the brown residue allowed

to stand overnight with dilute hydrochloric acid to remove the excess of aniline. After pulverization it was washed thoroughly with hydrochloric acid and water, and dried. To purify it a solution in chloroform was slowly poured, with constant stirring, into a large volume of ligroin, and after repeating this treatment several times a red amorphous product was obtained, which seemed to be free from tar, and was dried *in vacuo* for analysis:

I. 0.1393 gram substance gave 0.3109 gram CO_2, 0.0059 gram unburnt C and 0.0590 gram H_2O.

II. 0.2247 gram substance gave 14.6 cc. N_2 at 27°.2 and 759.2 mm.

	Calculated for $C_5H_3OH(C_6H_5NH)O_2$.	Found. I.	II.
C	65.03	65.10	....
H	4.43	4.71	....
N	6.90	....	7.16

What seemed to be the same product was formed by the action of aniline on the methoxy body, and of aniline, ether and alcohol on tribromanilinodiketocyclopentene, melting at 178°. A similar reaction, giving a different result, has been described already, in which aniline in alcoholic solution converted tetrabromdiketocyclopentene into the compound

$$C_5OH(C_6H_5NH)(C_6H_5N)O_2.$$

Properties of Anilinohydroxydiketopentene.—Red amorphous powder, which melts with decomposition at 140°. Easily soluble in alcohol, methyl alcohol, ether, chloroform, or acetone; slightly soluble in benzene, toluene, or water; essentially insoluble in ligroin. Strong hydrochloric acid has no visible effect on it; strong nitric acid, or sulphuric acid, forms a dark red solution with it. Sodic hydrate dissolves it, and the solution has a strong odor of phenyl isocyanide. Phenylhydrazine seems to have no action on it.

Action of Acetic Anhydride on the Anilinohydroxydiketocyclopentene.—Three grams of the compound

$$C_5H_2OH(C_6H_5NH)O_2$$

dissolved in acetic anhydride were warmed on the steam bath

for half an hour, after which the acetic anhydride was allowed to evaporate spontaneously. A chloroform solution of the residue was poured slowly, with constant stirring, into a large volume of ligroin, and after this process had been repeated several times the product was dried *in vacuo* for analysis:

0.1128 gram substance gave 5.95 cc. N_2 at 25° and 764 mm.

	Calculated for $C_5H_2OC_2H_3O(C_6H_5NH)O_2$.	Found.
N	5.71	5.92

Properties of Anilinoacetoxydiketocyclopentene, $C_5H_2OC_2H_3O(C_6H_5NH)O_2$.—An amorphous, pale brown powder, which melts with decomposition at 150°. Easily soluble in alcohol, methyl alcohol, chloroform, or acetone; moderately soluble in ether; slightly soluble in warm benzene or toluene; essentially insoluble in ligroin. Strong hydrochloric acid has no effect on it; strong nitric acid dissolves it slightly; strong sulphuric acid gives a dark green solution with it, whereas with the mother substance it gives a red solution. Sodic hydrate dissolves it with a strong odor of phenyl isocyanide. It is decomposed also by treating with water or ammonic hydrate.

Tribromtriketocyclopentene, $C_5HBr_3O_3$.—This substance was prepared by the method of Henle[1] as follows: Thirty-eight grams of crystallized sodic bromanilate were mixed with 160 cc. of water at the ordinary temperature and 12 cc. of bromine added slowly with shaking. When the evolution of carbonic dioxide had ceased, the excess of bromine was removed with acid sodic sulphite. Fifty grams of 30 per cent. sulphuric acid and 100 grams of sodic sulphate were then added and the solution extracted three times with 150 cc. of ether. Upon cooling the oily residue from the ether with ice water it solidified in small crystals, which were washed with benzene and crystallized from chloroform, when they showed the correct melting point, 191°.

Tetrabromdiketocyclopentene, $C_5Br_4O_2$.—Six and eight-tenths grams of the tribromtriketocyclopentene were warmed with phosphoric pentabromide according to Henle's directions,

[1] Ann. Chem. (Liebig), **352**, 45 (1907).

in an open dish on the steam bath, until the evolution of hydrobromic acid had ceased, when the product was poured upon ice, and then water added, and the mixture warmed to destroy the phosphoric oxybromide. The brown mass thus obtained was dissolved in strong nitric acid and precipitated with water, when yellow crystals were obtained which, after crystallization from benzene and ligroin, melted at 142°. To prove that the substance made in this way is identical with our product from tetrabromorthoquinone, it was converted into the methoxy derivative, which melted at 67°, and the ethoxy compound, which melted at 110°, showing that they were the same as the corresponding derivatives of our substance.

CAMBRIDGE, September 24, 1909.

STUDIES IN THE PREPARATION OF NITRILES.

BY E. EMMET REID.

In making a quantity of benzonitrile from benzoic acid and lead sulphocyanate according to the method of Letts and Krüss, some observations were made which led to considerable improvement in the yield obtainable and also to views, quite different from theirs, as to the mechanism of the reaction.

Historical.

In 1872 E. A. Letts,[1] of London, studied the action of potassium sulphocyanate on acids, using, particularly, a mixture of 180 grams (three molecules) of acetic acid to 100 grams (one molecule) of the salt, and boiling the mixture several hours. He found the main products to be acetamide and carbon oxysulphide. Some hydrogen sulphide and carbon dioxide were also found, but these he supposed to be due to a secondary reaction. He represented the reactions thus:

(1) $HCNS + C_2H_3OOH = C_2H_3ONH_2 + COS,$

and

(2) $C_2H_3ONH_2 + COS = CH_3CN + CO_2 + H_2S.$

In case of acetic acid he did not identify the nitrile, but with

[1] Ber. d. chem. Ges., 5, 669–74.

isobutyric acid and valeric acid he found both amide and nitrile, the amide being the main product.

With benzoic acid the nitrile was almost the sole product, only traces of the amide being found. In this case he represented the reaction by the equation

(3) $HCNS + C_7H_5OOH = C_7H_5N + CO_2 + H_2S$.

He actually used two molecules of benzoic acid to one molecule of potassium sulphocyanate, as one molecule of the acid was used up in setting free the sulphocyanic acid. Half of the benzoic acid was recovered from the residue. He reported the yield as 80 per cent. of the acid used up, or 40 per cent. of the total benzoic acid taken.

Pfankuch[1] heated barium benzoate with excess of barium sulphocyanate and got benzonitrile but mixed with large quantities of other products. Barium acetate and barium sulphocyanate gave similar results but the other products were in excess of the acetonitrile. Most of his effort was spent on the identification of the products other than the nitriles.

Kekulé[2] took up the question. He quotes Williams, who had repeated the work of Letts and of Pfankuch. This worker obtained smaller yields of nitriles than Letts reported, while Pfankuch's results were not entirely verified. Kekulé mentions work of Purper who heated benzoic acid with ammonium sulphocyanate and got benzamide. Kekulé recalls the fact that Letts had gotten amides from acids of the fatty series, but nitriles from benzoic and cinnamic acids, and asks why the reaction is different in the two series and also why ammonium and potassium salts react differently. He states the case thus: "The first molecule of acid gives sulphocyanic acid, which reacts with the second molecule of the organic acid, or on the ammonium salt of the acid, if ammonium sulphocyanate is used, so that acetamide and carbon oxysulphide are formed by double decomposition. Since, as was shown above, 1 molecule of ammonium sulphocyanate can change only 1 molecule of benzoic acid into amide, so it is

[1] J. prakt. Chem., [2] 6, 97.
[2] Ber. d. chem. Ges., 6, 111–4.

proved that, at least under these conditions, carbon oxysulphide does not act dehydratingly on ammonium benzoate to form benzamide. If, as Letts found, in the distillation of potassium sulphocyanate with 2 molecules of benzoic acid, nitrile is formed, this can result only from the dehydrating effect of potassium benzoate on benzamide, whereby the nitrile is formed. A special experiment, in which 12 grams benzamide were distilled with 17 grams potassium benzoate and yielded 8 grams benzonitrile, proved the correctness of this view." Müller found that on rapid distillation the amide was obtained. Kekulé thought that the amides of the fatty series were more difficult to dehydrate by the corresponding potassium salts than were the aromatic amides.

G. Krüss[1] complained of the yield in Letts' process and improved the method by substituting lead sulphocyanate for the potassium salt. His idea was that the hydrogen sulphide first evolved would act with the unchanged lead sulphocyanate to free the sulphocyanic acid, and less of the benzoic acid would be required for this purpose. Lead sulphide instead of the benzoate would be left in the retort and all of the benzoic acid put in might take part in the nitrile formation. "On account of the instability of lead sulphocyanate, at high temperatures, an excess was always used." He gives no intimation as to how much excess he used. Schöpff,[2] in making brombenzonitriles, used over twice as much of the lead sulphocyanate as is called for by the equation. Krüss reports yields of 50 to 55 grams benzonitrile from 100 grams of benzoic acid, or double what he was able to obtain by the method of Letts. He gives the equation

$$(4)\quad 2C_6H_5COOH + Pb(CNS)_2 = 2C_6H_5CN + PbS + H_2S + 2CO_2.$$

Tingle[3] made a comparative study of this and other methods of preparation of benzonitrile with reference to the cost of materials and time required.

General and Theoretical.

In making a quantity of benzonitrile according to the

[1] Ber. d. chem. Ges., **17**, 1760–9.
[2] *Ibid.*, **23**, 3435–40.
[3] THIS JOURNAL, **35**, 87.

method of Krüss the yield was not found satisfactory. In one experiment the gas evolved was passed through lead acetate solution and the precipitate obtained appeared insignificant compared with the amounts of reagents in the retort. This led to the following quantitative experiment:

Into a small distilling bulb the outlet of which entered a small U-tube standing in a beaker of cold water were weighed, 4.884 grams of benzoic acid and 6.466 grams lead sulphocyanate. The gas issuing from the other side of the U-tube was passed through a large and a small flask of acidulated lead acetate solution and then through a large and a small flask of barium hydroxide solution, the latter being protected by a wash bottle of caustic soda. During the experiment purified air was slowly aspirated through the whole system. The tube which admitted the air to the reaction flask reached nearly to the surface of the mixture. The flask was heated in a bath. At 197° the reaction had begun. During 30 minutes the temperature was raised gradually to 226°. At the end of this time there seemed to be no further action. The nitrile obtained weighed 1.476 grams, or 36 per cent. of the calculated amount. The lead sulphide collected from the two flasks weighed 0.033 gram, corresponding to 0.0047 gram hydrogen sulphide, or 0.68 per cent. of the theoretical. The barium carbonate weighed 3.432 grams, correspondlng to 0.765 gram carbon dioxide, or 43 per cent. of the calculated.

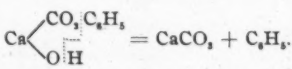
The fact that such a small amount of hydrogen sulphide was evolved suggested that it might in some way be involved in the formation of complex products. High-boiling products had been noticed by Pfankuch.[1] Williams had obtained products boiling at 220°–245° and 245°–275°. In order to avoid the formation of hydrogen sulphide, lead benzoate was substituted for the benzoic acid. Pfankuch and Williams[2] had both used a mixture of salts, but had used barium benzoate and barium sulphocyanate, with the latter in large excess. Their results were poor as regards the yield of nitrile. Experi-

[1] J. prakt. Chem., [2] 6, 97.
[2] Ber. d. chem. Ges., 6, 111–4.

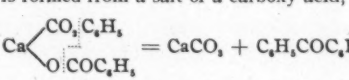
ment proved that the mixture of lead benzoate and lead sulphocyanate did give a satisfactory yield of benzonitrile.

While little is known of the mechanism of such pyrogenetic reactions, yet it is interesting to compare this with several other reactions which take place under similar circumstances with more or less similar substances. For convenience, a mixture of salts is written as a mixed salt.

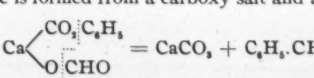
A hydrocarbon is formed from a salt of a carboxy acid and lime,



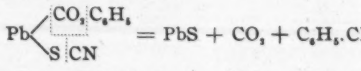
A ketone is formed from a salt of a carboxy acid,



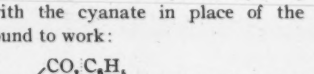
An aldehyde is formed from a carboxy salt and a formate,



Since lead benzoate and lead sulphocyanate give the nitrile under the same conditions it seems not amiss to write the reaction in the same way, remembering, however, that the thiocarbonate would break up.



This equation suggested the possibility of getting a similar reaction with the cyanate in place of the sulphocyanate. This was found to work:



The fact that sulphocyanates are formed from cyanides by the addition of sulphur suggested the idea of using a cyanide and sulphur in place of the sulphocyanate. This was found to work well, but whether the sulphocyanate is formed as an

intermediate product or not has not been found out. It may be represented simply in this way:

$$S + Pb\begin{cases}CO_2.C_6H_5\\ \vdots\\ CN\end{cases} = PbS + CO_2 + C_6H_5.CN.$$

The fact that a nitrile is formed from a sulphonate and a cyanide on fusion,

$$Ca\begin{cases}SO_3.C_6H_5\\ \vdots\\ CN\end{cases} = CaSO_3 + C_6H_5.CN,$$

suggested that a nitrile might be formed also from a carboxy salt and a cyanide in the same manner. Experiment has shown that some nitrile and carbon monoxide are formed, but the amount and apparent complexity of the by-products of the reaction indicate that it is not as simple as the following equation would indicate:

$$Pb\begin{cases}CO_2.C_6H_5\\ \vdots\\ CN\end{cases} = PbO + CO + C_6H_5.CN.$$

Lead, sodium, zinc, and barium benzoates have been studied with potassium cyanate, lead cyanate, potassium sulphocyanate, lead sulphocyanate, barium sulphocyanate, lead cyanide and sulphur, lead ferrocyanide and sulphur, zinc ferrocyanide and sulphur, potassium ferrocyanide and sulphur, silver cyanide and sulphur, and lead ferrocyanide without sulphur.

All of the combinations of the above which have been tried have given considerable yields of nitriles, the amount of the yield varying with circumstances. The yield is doubtless mainly dependent on the melting point of the compounds and the temperature at which they decompose. High-melting compounds may be largely decomposed before they come into efficient contact with the other reagents. A high reaction temperature favors side reactions. Salts of weak bases may be partly decomposed while being dehydrated previous to use, or may be decomposed by water present during the reaction itself. The cyanates did not give good yields, apparently for the reason that the oxygen of the cyanate caused the combustion of some of the organic acid.

Those who have worked on this reaction have supposed that it took place solely between the molecules of the two acids in the free state. Since the benzoic acid would form lead benzoate with a portion of the lead sulphocyanate, the two salts would be present during the reaction as well as the two acids. Hence the results of previous workers may be interpreted just as well on the assumption that the reaction takes place between the salts. The results of the present experiments, in which only salts were present, can be explained in only the one way, namely, that the reaction takes place between the salts. The fact that, in the method of Krüss, one-half of the lead sulphocyanate was needed to form lead benzoate with which the other half of the sulphocyanate was to react explains why the yields were about 50 per cent. Krüss and those who have used his method have sometimes brought the yield somewhat above 50 per cent. by using an excess of the sulphocyanate. Tingle used two equivalents of lead sulphocyanate to one equivalent of benzoic acid. Since free sulphocyanic acid is extremely unstable at high temperatures it would be driven out almost quantitatively by the benzoic acid till there would be in the retort a mixture of equivalent quantities of lead benzoate and lead sulphocyanate. This is just the mixture which was put into the retort in some of the present experiments. The yield of 71 per cent., recorded by Tingle from his mixture, agrees well with that here obtained from a mixture of the salts. The presence of a large excess of the lead sulphocyanate makes the mass more difficult to fuse and seems to favor side reactions.

Several substituted benzoic acids have been tried. The three aminobenzoic acids gave only small quantities of distillates which, on account of their apparent complexity, seemed not worth working up. Aniline was proved to be present in considerable quantity in the case of the ortho compound. *p*-Nitrobenzoic acid was tried in the form of its lead salt with lead sulphocyanate, but exploded on heating. Meta- and parabrombenzoic acids gave good results. There seems to be every reason to think that the method as given below would be readily applicable to a number of the aromatic acids.

Some work has been done on acids of the fatty series and it is certain that the reaction takes place in much the same way but the detailed study of the conditions, yields, etc., must be left for another paper.

Experimental.

Materials.—Though all of the materials used have been made and described long ago, the scarcity of information concerning some of them warrants the insertion of some details.

The most of the lead benzoate used was made by precipitation. Benzoic acid was dissolved in water with the addition of ammonia or caustic soda to exact neutrality and to this was added a solution of the calculated amount of lead nitrate. The solutions must not be hot, though they may be warm, since in hot water the lead benzoate partially melts or masses together into a sort of dough. The precipitate was filtered and well washed. It is so nearly insoluble in water that the mother liquors may be thrown away and the salt thoroughly washed. The air-dry salt was dehydrated in a porcelain dish over a free flame. It must be stirred constantly. At about 100° it gets pasty and begins to give off water. At higher temperatures it softens more and more and continues to give off water. At 150° the most of the water is gone and the salt is thoroughly liquid. It was usually heated to about 210°. It was then poured out on a slate table and subsequently powdered. The fused salt forms a perfectly transparent, more or less amber colored, brittle mass.

The same salt was also made by direct fusion of benzoic acid and lead oxide. For this purpose the acid was melted in a dish and the calculated amount of lead oxide sifted in with constant stirring. The mass was stirred constantly and the temperature gradually raised to about 210°. A few particles of metallic lead are formed and the color of the fused mass is somewhat darker than that made in the other way. This is a very rapid and convenient way of making the salt. The product, when powdered, is practically white. The salt made in this way was used in experiments 8, 9, 11, and 12.

Whichever method is used, the dehydrated salt probably

still contains some water and has certainly lost some benzoic acid. In the calculation of yields, however, it was considered as having the theoretical composition.

Zinc benzoate, recently studied by Parietta,[1] can not be made by the fusion method as its melting point is too high. When made by precipitation a considerable amount, about 14.5 grams per liter at 59°, remains in the solution. The precipitated salt is best filtered hot. It is anhydrous and may be dried at 200° in an air bath without softening or caking together.

Barium and sodium benzoates were made by direct neutralization and evaporation. Both were dried at high temperatures.

Liebig made lead sulphocyanide and described it as "yellow crystals." It was made by precipitation from fairly dilute, moderately warm, neutral solutions of equivalent quantities of ammonium sulphocyanate and lead nitrate. In one preparation specially pure salts were used and the product was washed with water, alcohol, and ether. It dried rapidly and remained a pure white, except that when it was exposed to light it turned a little dark on the surface. The bulk of the salt used in this work was decidedly yellow after drying and standing some time. The salt is anhydrous and may be dried at 140° without appreciable decomposition.

The lead and zinc ferrocyanides and the lead and silver cyanides were made by precipitation from neutral solutions. The lead ferrocyanide proved difficult to dehydrate. It lost water only slowly at 160°. It was heated to 200° for eight hours in a Kjeldahl flask, the neck of which slanted down and projected from the air bath. Access of air was nearly cut off by a stopper carrying a tube. The salt takes fire at about this temperature when heated in open air. The zinc ferrocyanide was dehydrated in the same way.

Method of Work.—The dry powders were well mixed and put into a plain retort. The neck of the retort was connected with a half-inch tube about two and a half feet long which

[1] Gaz. Chim. Ital., 36, II, 67–70.

reached nearly to the bottom of a flask, one-half to one liter in size. In the later experiments a plug of cotton was put in the neck of this flask to aid in retaining the fumes, and the gases were led into a second empty flask. In this way a few drops of nitrile were found in the second flask. For an amount of salts equivalent to 122 grams of benzoic acid a 250 cc. retort was used. Smaller retorts were used with the smaller amounts of materials. The retort may be nearly filled with the dry mixture. In no case was much trouble caused by foaming, though the burner was held in the hand and, during the first part of the reaction, the heat was applied to the side of the retort so as to keep the reaction under control. The time of heating was from thirty minutes to a little over an hour. A single Bunsen burner was used except that sometimes an extra large burner was used to finish the reaction. When the heat is applied the mass melts and bubbles of gas and fumes begin to come off at once. In some experiments the nitrile began to drop from the end of the retort neck within two minutes after the flame was applied. The reaction usually proceeds regularly and spreads through the whole mass which becomes more or less liquid throughout. At the end the residue melts down into a cake and the nitrile ceases to come off.

Method of Examination.—The methods of separation of the constituents of the crude distillate were only such as are used in ordinary organic preparations. The aim has been to find and report such quantities as might readily be obtained with the simplest possible apparatus and the least outlay for time and chemicals. The question has not been so much what amount of nitrile is formed in a given reaction, but what amount can be simply and profitably obtained by such reaction.

The distillate from the retort was treated with an equal volume of water and enough ammonia to cause it to smell of the gas. This mixture was distilled with steam. For mixtures yielding 40 to 75 grams of nitrile a flask from 700 to 1000 cc. in size was used as a receiver. A handful of salt was put into the flask with enough water to wet it. The distillate

was caught in this till the flask was three-fourths or more full. The mixture was shaken to dissolve the bulk of the salt and then brine poured in till the nitrile was driven up into the neck of the flask. After standing a while in a cool place the nitrile was pipetted off and weighed. The last small portion of nitrile in the neck of the flask was diluted with a little ether and removed. This was warmed in a beaker to expel the ether and to the main portion. In some of the later experiments the added contents of the flask were extracted with ether. In a special experiment 65.9 grams of benzonitrile were distilled with steam and recovered in this manner; found, 62.8 grams, showing a loss of 3.1 grams. On the other hand the nitrile was not dried before weighing. This error partially balanced the other.

The residue in the flask after the steam distillation was filtered hot and what was left on the funnel was set down as "tar." Benzophenone was sought for in this tar but was not found. Usually long needles separated from this filtrate on cooling. These were sometimes an inch or so in length and of a pale yellow color and silky appearance. These varied in appearance and color but were usually of this description. They are put down in the results as "needles." Specimens of these needles have since been treated with strong caustic soda solution. This separates them into two compounds, one of which is not soluble in caustic soda and the other of which is precipitated from its caustic soda solution by the addition of ammonium chloride. For the present, these are designated as compounds A and B.

Compound A.—This is insoluble in caustic soda, melts at 138°, dissolves in 140 parts of boiling water, and separates from such solution in perfectly white needles, often an inch in length. Sometimes it has been obtained in pearly white scales with the same melting point. It distils near 280°, is slightly volatile with steam, and gives ammonia when heated with strong alkali.

Compound B.—This is a very weak acid as it dissolves in strong caustic soda but not in ammonium hydroxide. It is soluble in 230 parts of boiling water and separates from this

solution in long slightly straw-colored needles. It melts at 230° and gives ammonia when heated with strong alkali.

These two compounds are still under investigation.

The filtrate from these needles was acidified to obtain the benzoic acid. Ammonium benzoate loses a small part of its acid on distillation with steam. In a special experiment 1.7 grams out of 35 grams were lost in this way. Beginning with experiment 11, the original crude product was, in most cases, extracted with soda solution to obtain the acid.

The results are collected below in tabular form, the experiments being given in practically the same order in which they were made. The later ones are more trustworthy. All weighings were made on a balance barely sensitive to 0.1 gram.

The yield of benzonitrile is calculated on the total benzoic acid supposed to be in the salt used. In cases in which much of the acid was recovered the "net" yield of nitrile is also calculated. This is based on the amount of benzoic acid which disappeared during the reaction. The yields found are supposed to be considerably less than the amounts formed.

Where two numbers are given under the heading "time" the lower figures give the time during which the retort was heated with an extra large burner after it had been heated with the ordinary burner for the time given by the upper figures.

The figures in the first column, under the formulae of the constituents of the mixture, represent the weights used in grams. Under these are placed the gram-equivalents of the substances used.

No.	Composition of mixture.			Time in min.	Crude prod.	Nitrile. Calc.	Nitrile. Found.	Needles.	Tar.	Acid recov.	Yield. Per cent.	Net yield. Per cent.
1	$K_4Fe(CN)_6$,	S,	$Pb(C_6H_5CO_2)_2$,	...	18.6	25.7	12.1	...	...	....	47	....
	15	8	62.3									
2	$Pb(CN)_2$,	S,	$Pb(C_6H_5CO_2)_2$,	...	47	82.4	12.5	...	5	8	15	....
	105	26	180									
	0.8	0.8	0.8									
3	$Pb_2Fe(CN)_6$,	S,	$Pb(C_6H_5CO_2)_2$,	60	98	98	63.3	1	1.5	16	64	75
	110	33	212									
	1.1	1.1	1									
4	$Pb_2Fe(CN)_6.3H_2O$,	S,	$Pb(C_6H_5CO_2)_2$,	30	51.8	49.2	24.6	0.5	2.0	17.5	50	71
	59.3	18	107									
	0.55	0.55	0.5									
5	KCNO,		$Pb(C_6H_5CO_2)_2$,	...	13	25.7	....	...	...	....	low	....
	20		62.3									
	0.25		0.25									
6	$Pb(CNO)_2$,		$Pb(C_6H_5CO_2)_2$,	...	13	23.2	11.1	...	...	0.0	48	....
	32.5		59.3									
	0.23		0.26									
7	$Pb(CNS)_2$,		$Pb(C_6H_5CO_2)_2$,	30	82	97	60	0.0	3	7.0	62	66
	153		212									
	0.95		0.95									
8	$Pb(CNS)_2$,		$Pb(C_6H_5CO_2)_2$,	58	65	69	46.3	...	...	7.0	68	74
	150		150									
	0.88		0.66									
9	$Pb_2Fe(CN)_6$,	S,	$Pb(C_6H_5CO_2)_2$,	...	90	97	66	.3	1	15.0	68	78
	114.6	33	212									
	1.08	1.03	0.95									

No.	Composition of mixture			Time in min.	Crude prod.	Nitrile. Calc.	Nitrile. Found.	Needles.	Tar.	Acid recov.	Yield. Per cent.	Net yield. Per cent.
10	$AgCN$,	S,	$Pb(C_6H_5CO_2)_2$,	30	23.5	19.3	10.2	...	...	5.5	53	70
	25.2	15	42									
	0.19	0.5	0.18									
11	$Pb_2Fe(CN)_6$,	S,	$Pb(C_6H_5CO_2)_2$,	70	71.6	82.4	48.3	1.3	1.3	9.3	58.6	65
	90	28	180									
	0.88	0.88	0.80									
12	$Pb_2Fe(CN)_6$,	S,	$Pb(C_6H_5CO_2)_2$,	45	78.5	82.4	49.8	7.5	...	9.6	60	66
	104.3	32	179.6									
	0.8	0.8	0.8									
13	$Pb_2Fe(CN)_6$,	S,	$Pb(C_6H_5CO_2)_2$,	23	78.6	82.4	52.6	2.1	...	13.3	64	74
	91	28	180	7								
	0.88	0.88	0.80									
14	$Pb(CNS)_2$,		$NaC_6H_5CO_2$,	31	58.3	82.4	47.0	0.0	...	0.5	57	....
	161.5		115.2	20								
	1.0		0.8									
15	$Pb(CNS)_2$,	PbO,	$Pb(C_7H_5O_2)_2$,	41	79.9	82.4	53.3	...	...	9.0	65	75
	161.5	25	179.6									
	1.0	0.23	0.8									
16	$Zn_2Fe(CN)_6$,	S,	$Pb(C_7H_5O_2)_2$,	33	84.9	82.4	47.5	0.7	1.7	23.2	57	80
	50.2	28	179.6	8								
	0.88	0.88	0.80									
17	$Pb(CNS)_2$,		$Zn(C_7H_5O_2)_2$,	30	77.0	82.4	....	0.5	2.5	6.3	86	91
	161.5		122.8	6								
	1.0		0.8									

No.	Composition of mixture.			Time in min.	Crude prod.	Nitrile. Calc.	Nitrile. Found.	Needles.	Tar.	Acid recov.	Yield. Per cent.	Net yield. Per cent.
18	$Pb_2Fe(CN)_6$,	S,	$Zn(C_7H_5O_2)_2$,	25	69.5	72.1	44.5	5.0	3.0	10.6	65	74
	80	28	107.5	8								
	0.77	0.88	0.7									
19	$Pb_2Fe(CN)_6$,		$Pb(C_7H_5O_2)_2$,	24	53.6	67	43.9	1.0	3.5	1.0	62.5	...
	67.8		145.9	4								
	0.65		0.65									
20	$Pb(CNS)_2$,		$Zn(C_7H_5O_2)_2$,	25	66.9	72.1	54.4	0.5	1.6	4.0	75.4	79
	113.0		107.6	12								
	0.7		0.7									
21	$Ba(CNS)_2$,		$Ba(C_7H_5O_2)_2$,	22	60	82.4	48.9	...	7.9	0.0	59	...
	101.4		151.8	28								
	0.8		0.8									
22	$Pb_2Fe(CN)_6$,		$Zn(C_7H_5O_2)_2$,	54	35.1	66	22	...	...	...	33	...
	66.8		98.3	14								
	0.64		0.64									

Remarks on the Experiments.

Experiment 4.—This was made to test the effect of the presence of water in the mixture. The lead ferrocyanide, which contains 3 molecules of water, was used in air-dry condition. The yield is cut down considerably.

Experiment 5.—Unusually high temperature required and charred residue left in the retort. Free ammonia in the distillate.

Experiment 10.—Since silver cyanide frequently gives isocyanides and has been thought to have the constitution Ag-NC, the purpose of this experiment was to find whether it would yield such a product in this reaction. On account of the known instability of phenyl isocyanide at high temperatures and of its known tendency to combine with sulphur, an extra amount of sulphur was put in so as to form phenyl mustard oil in case the isocyanide were present at any time during the reaction. On distillation of the 10.2 grams of nitrile obtained in this experiment, 1.5 grams went over below 185° and 7.7 grams between 185° and 212°. The remainder, about one gram, was mixed with aniline, warmed, and stirred, but no formation of thiocarbanilide was observed. With fuming nitric acid it gave no test for sulphur.

Experiment 11.—In this the amount and nature of the gases evolved were studied also. From the usual receiver the gases were passed through acidified lead acetate and then through three flasks of strong caustic potash solution, then into an aspirator bottle which was full of water at the beginning of the experiment; 1800 cc. of gas were obtained. As practically all of this was collected during the first part of the experiment when the air was being driven out of the apparatus and as the amount corresponds quite well with the volume of the retort and receivers which were left full of carbon dioxide instead of the air which they originally contained, it is evident that only carbon dioxide was given off. No hydrogen sulphide was found. The carbon dioxide found was 24.2 grams, or 68.8 per cent. of the calculated.

Experiment 12.—The carbon dioxide was weighed in this also and was found to be 79.7 per cent. of that calculated on

the total benzoic acid supposed to be in the retort, but in this experiment 10 per cent. of the acid was recovered. Hence the carbon dioxide found was 88.5 per cent. of that calculated from the benzoic acid actually taking part in the reaction.

Experiment 16.—This was to test the suitability of zinc ferrocyanide for use in place of lead ferrocyanide. While the net yield is raised, there is no improvement on the whole.

Experiments 17 and 18.—These were made to compare zinc benzoate with lead benzoate. There is a marked improvement in the yield. These two experiments show the best method for making benzonitrile. On account of the greater ease in obtaining lead sulphocyanate in the dry condition as compared with the ferrocyanide, experiment 17 represents the best laboratory method. For factory use the cheapness of the ferrocyanides may give the preference to the method of experiment 18. The retort was unharmed in both experiments.

Experiment 20.—This, as compared with No. 17, shows that a slight excess of the lead sulphocyanate is desirable.

Experiments 19 and 22.—These were made to test the utility of the sulphur commonly added. They show that the addition of the sulphur to the ferrocyanides is a decided advantage. The yields are better with the sulphur and the reactions take place at more moderate temperatures and go more smoothly.

Experiment 21.—This was made to test the salts used by Pfankuch. An extremely high temperature is required. The retort was thoroughly blistered and a large amount of tarry products was formed. The difficulty seems to be in the high melting points of the barium salts. A considerable amount of free ammonia was in the distillate. The nitrile obtained by the usual steam distillation was slightly fluorescent and, on fractionation, gave an unusually large amount, 15 per cent., of liquid boiling above 192°.

Experiment 22.—In this case the carbon dioxide produced was weighed and found to be 24 grams out of a possible 28 grams. The remaining gas contained 1 or 2 grams of carbon monoxide. So far there is no way of deciding whether carbon dioxide results from the oxidation of carbon monoxide originally

produced according to the equation given above, or whether the carbon dioxide is the original product. A highly complex mass was left in the retort.

The Benzonitrile Produced.—The products of experiment 11 to 20 were fractionated separately. On the first distillation, on the average, 16 per cent. went over below 186° and 75 per cent. between 186° and 192°, leaving 8 per cent. of residue. Further examination showed that the lower fractions were benzonitrile containing a little alcohol and ether. The residues above 192° proved to be mainly benzonitrile mixed with a small quantity of tarry products and a little of compound A mentioned above.

On refractionating the residues from 870 grams of crude nitrile, 26 grams of product boiling above 192° was obtained. From the 6 gram fraction of this boiling between 275 and 300°, 1.65 grams of compound A was obtained by drying the pasty mass on a porous plate.

Substituted Benzoic Acids.

As noted above, the three aminobenzoic acids do not give nitriles according to this method. The nitrobenzoic acids give explosions. Salicylic acid and phthalic acids give complicated products. All of these present special difficulties.

Lead *m*-brombenzoate (27.5 grams) was distilled with 20 grams (1.33 equivalents) lead sulphocyanate. The crude product weighed 13.0 grams, from which 1.2 grams of the acid was recovered. The remainder was distilled with steam and yielded 9.25 grams of the nitrile in good condition. This is 60 per cent. of the calculated.

Similar yields were obtained with lead *p*-brombenzoate, whether distilled with lead sulphocyanate or with lead ferrocyanide and sulphur. The distillation of *p*-brombenzonitrile with steam was found to be tedious and wasteful. Recrystallization from alcohol gave a purer product with less loss. Schöpff used over two equivalents of lead sulphocyanate in making the brombenzonitriles by the method of Krüss and reported 45 and 33 per cent. yields, respectively, for the meta and para nitriles.

Preparation of Benzonitrile.

As a laboratory method of preparing benzonitrile the following is suggested: To a hot solution of 50 grams of caustic soda in 400 cc. of water, 150 grams of benzoic acid are added. The solution is carefully neutralized by the addition of ammonia or soda solution. One hundred and eighty grams of zinc sulphate are dissolved in 400 cc. of hot water. The two solutions are well mixed and the precipitated zinc benzoate filtered off hot. This is washed several times and spread out on a paper to dry. When air-dry it is heated to 200° for several hours in an air bath. The mother liquor from the zinc benzoate may be concentrated and acidified for the recovery of some of the benzoic acid.

One hundred and seventy-five grams lead nitrate (or 200 grams lead acetate) are dissolved in 500 cc. warm water and 80 grams of ammonium sulphocyanate are likewise dissolved in 500 cc. water, and the two solutions mixed. The precipitated lead sulphocyanate is washed well with water and then twice with alcohol. It is spread on paper to dry. When air-dry, it may be further dried by heating for several hours from 120° to 140°.

To 120 grams of the dried zinc benzoate are added 160 grams of the lead sulphocyanate. The two are thoroughly mixed by grinding together in a mortar. The mixture is put into a 250 cc. plain retort which is connected by an air condenser with a dry one-liter flask. The retort is heated with a Bunsen burner held in the hand. The heat is applied first at the side of the retort, one portion being heated at a time. Sufficient heat should be applied to keep the reaction going well though care must be taken to avoid foaming over. When the reaction gets slow more heat is applied. An extra burner may be used. The retort is heated as long as any liquid goes over. A high temperature is required towards the end. The retort may be cleaned with nitric acid.

The nitrile is obtained from the distillate by treating with ammonia, distilling with steam and salting out as described above.

Conclusions.

1. The best laboratory method for the preparation of benzonitrile is to distil dry zinc benzoate with dry lead sulphocyanate.

2. A mixture of equivalent quantities of lead ferrocyanide and sulphur may be used in place of the sulphocyanate.

3. The formation of benzonitrile under these conditions takes place substantially according to the following equation:

$$Pb\begin{matrix}CO_2C_6H_5\\SCN\end{matrix} = PbS + CO_2 + C_6H_5CN.$$

4. Ferrocyanides may sometimes in organic synthesis be substituted for cyanides.

It is desired to reserve the study of this reaction in the fatty series for further work.

JOHNS HOPKINS UNIVERSITY.

OBITUARIES.

LUDWIG MOND.

By the death, in London, on December 11, 1909, of Dr. Ludwig Mond, chemistry lost one to whom she will ever be indebted, for not only by his personal talent and labor, but also by generous and unstinted use of his large fortune, he has contributed largely to the advance of the science. The "International Catalogue of Scientific Literature" and the Davy-Faraday Laboratory are enduring monuments to his memory, and his benefactions to other institutions and even individuals are numberless.

Born in Cassel on March 7, 1839, Mond received his preparatory instruction in the schools of that city. He then went to Marburg, where he studied under Kolbe, and from there to Heidelberg to pursue his studies in Bunsen's laboratory. After graduating, he at once turned his attention to technology and for four years was connected with different German and Dutch factories, sometimes as analyst, sometimes as director. In 1862, having developed and patented a process for recovering the sulphur from the alkali-waste obtained as by-product in the manufacture of soda by the LeBlanc method, he went to

England to introduce his process in the great alkali works of that country. It was adopted by several manufacturers and Mond, after erecting and for a short time managing a LeBlanc soda factory in Holland, returned to England and settled down to the business of making alkali.

In the meantime the Solvay brothers had worked out their ammonia-soda process, and Mond was so impressed by its possibilities that he determined to risk his little capital in securing a license to work it in England. With the coöperation of Mr. (now Sir) John T. Brunner, under the firm name of Brunner, Mond & Co., a factory was erected at Winnington in Norwich which was destined to become one of the largest of its kind in the world, until it now employs 4000 men. Its great success was in large measure due to Mond. He displayed great skill in overcoming difficulties and introducing improvements, such as increasing the efficiency of the coal used as fuel by the formation of Mond gas and the recovery of the nitrogen as ammonia. In this connection he was led to investigate the action of carbon monoxide on metals, which resulted in the discovery of the metallic carbonyls and of a new process of extracting nickel from its ores which is now widely used. The occlusion of gases by the platinum metals also engaged his attention.

Besides endowing the Davy-Faraday Institute, he made liberal donations to the Royal Institution, Cambridge, Liverpool and Manchester Universitie, University College, London, and the Lister Institute. Being compelled, in the last 20 years, through ill health, to spend his winters in Rome, he became interested in the chemical institute of the University there, an interest of which he gave very material proofs. An intimate friend of Canizzaro, he last year founded a prize bearing that scientist's name, and in the same year contributed munificently to the establishment of the Chemische Reichsanstalt.

He was deeply interested in art, and his collection of paintings, accumulated during his visits in Italy, is one of the most valuable in England.

His merits as a scientist were widely recognized: he held honorary degrees from many universities, was a Fellow of various scientific societies, president of the Society of Chemical Industry in 1888–1889 and of the chemical section of the British Association in 1896. He was recently offered the presidency of the Chemical Society but was compelled to refuse the honor on account of ill health.

CHARLES BENJAMIN DUDLEY.

Dr. Charles Benjamin Dudley, chief chemist of the Pennsylvania Railroad Company, died at his home in Altoona on December 21, 1909.

A short account of Dr. Dudley's life and of the services he has rendered to chemistry and technology will be published in the next number of THIS JOURNAL.

REVIEWS.

THE GENERAL CHARACTERS OF THE PROTEINS. By S. B. SCHRYVER, PH.D., D.SC., Lecturer on Physiological Chemistry, University College, London. London, New York, Bombay and Calcutta: Longmans, Green and Co. 1909. pp. x + 86.

This book appears to be carefully compiled but the fact that the majority of the subjects discussed do not lend themselves to more than a superficially exact treatment naturally detracts from the interest of the work. It may well be, however, that a clear exposition of the obvious deficiencies in our store of facts may stimulate further research. The subject matter is divided into sections on the general, physical and chemical properties of the proteins, together with a short account of the newly developed biological methods for the identification and differentiation of proteins. Each of the essays is provided with a useful bibliography. H. D. DAKIN.

OUTLINES OF PHYSICAL CHEMISTRY. By GEORGE SENTER, PH.D., B.SC., (Lond.). London: Menthuen & Co. 1909. pp. xvii + 369. Price, 3s. 6d.

The purpose of the author may be gathered from his statement in the preface: "I have preferred to deal in considerable detail with those branches of the subject which usually present most difficulty to beginners, such as the modern theory of solutions, the principles of chemical equilibrium, electrical conductivity and electromotive force, and have devoted relatively less space to the relationships between physical properties and chemical composition." There are frequent references to the literature, and the various sections are closed by excellent "practical illustrations." The presentation is exceptionally clear. The author rides no particular hobby, so that the viewpoint is orthodox and thus calculated to fit the need of the average teacher. The mathematics used is of the simplest possible nature.

There are a few mistakes. On page 110, line 9, we find "solute" for "solution," and at the bottom of page 223 "cath-

ode" and "anode" should be transposed. The use of Q for different quantities on pages 135 and 315 might confuse the beginner. On page 227 we read the astonishing statement that, "if in an hour a gram equivalent of sodium and of chlorine are discharged at the respective electrodes, the current which has passed through the cell is $2 \times 96540 \div 3600 = 53.6$ amperes," *i. e.*, a faraday for each ion.

The moderate price is an attractive feature in view of the heavy outlay of the scientific student for books, and the frequency of new editions to keep pace with rapid advance of this branch of science. In the opinion of the reviewer, the book is one of the best elementary texts that have appeared, and deserves a cordial welcome. JOEL H. HILDEBRAND.

LES BASES PHYSICO-CHIMIQUES DE LA CHIMIE ANALYTIQUE. PAR LE DR. W. HERZ, Professeur à l' Université de Breslau. Traduit de l' allemand par E. PHILIPPI, Licencié ès Sciences. Paris: Gauthier-Villars. 1909. pp. 167.

The scope of this little book can be seen best from its contents. The twelve chapters and an introduction deal with: The Gas Laws, Theory of Solutions, Abnormal Molecular Weights, Theory of Electrolytic Dissociation, Law of Electroneutrality of Solutions, Ionization and Physical Properties, Colloidal Solutions, Solid Solutions, Chemical Mechanics, Law of Mass Action and Electrolytic Dissociation, Heterogeneous Systems, The Different Phases in a Heterogeneous System, and Velocity of Reaction in a Homogeneous System.

The book is clearly written and will doubtless prove to be useful in the field which it is meant to cover. H. C. J.

A MANUAL OF VOLUMETRIC ANALYSIS FOR THE USE OF PHARMACISTS, SANITARY AND FOOD CHEMISTS, AS WELL AS FOR STUDENTS IN THESE BRANCHES. BY HENRY W. SCHIMPF, PH.G., M.D., Professor of Analytical Chemistry, Brooklyn College of Pharmacy, etc., etc. Fifth Edition, Revised and Enlarged. New York: John Wiley & Sons; London: Chapman & Hall, Ltd. 1909. pp. xx + 725, 102 Figures. Price, $5.

The earlier editions of this text-book are well-known to many analysts, especially to pharmacists, for whom they have been mainly prepared. The present edition is the result of an extensive revision and enlargement, to give it the character of a "Manual" of volumetric analysis. Part I opens with a series of chapters on such general topics as indicators (an exhaustive discussion), apparatus, and methods of calculation, and are followed by chapters on neutralization methods, precipitation methods, and oxidation and reduction processes. Part II includes chapters on the volumetric methods for the

determinations of the common organic and inorganic acid radicals and of each of the more common metals. Part III treats of sanitary analyses and the volumetric analysis of organic medicinal substances. Part IV deals with a few gasometric methods, and the book closes with a most complete index, covering more than twenty-six pages.

Like the former editions, the manual in its present form is prepared with the needs of the pharmacist chiefly in mind and no pains are spared to make many points clear to those analysts, who, as a rule, are not able to spend any considerable amount of time in the preliminary study of chemistry as such. This is particularly true with reference to equations and the calculation of results of analysis and there is an almost unnecessary repetition of simple directions and statements throughout the book. A considerable variety of procedures are outlined for nearly every determination, but it is at least open to question whether a smaller number more fully and occasionally more accurately described would not have been more valuable as a guide. In some instances, as for example the standardization of a solution of sulphuric acid by precipitation of barium sulphate on page 73, the directions given are wholly inadequate to secure accurate results. As a whole, however, the book in its present form is likely to prove useful. It is well printed, and well provided with references to original articles bearing upon the procedures cited. H. P. TALBOT.

LABORATORY METHODS OF INORGANIC CHEMISTRY. By HEINRICH BILTZ, University Kiel, and WILHELM BILTZ, University Göttingen. Authorized translation by WILLIAM T. HALL and ARTHUR A. BLANCHARD, Massachusetts Institute of Technology New York: John Wiley & Sons; London: Chapman & Hall, Ltd. 1909. pp. xv + 246. Price, $3.

This volume is the largest and best book on inorganic preparations yet published. It is not a mere collection of recipes like many manuals. The one hundred and sixty-one preparations are used as illustrations of some law or special method; for example, the chapter on elements includes reduction processes by carbon, by aluminothermy, by potassium cyanide and by aqueous reducing agents, desulphurization of sulphides by the precipitation and roasting processes, cupellation and preparation of metals by electrolysis, each with illustrative preparations. Under allotropy the allotropic silver sulphide and sulphur and the transformation points of cuprous and silver mercuro-iodides are shown. The passive state is studied in passive iron, the amorphous condition in amorphous sulphur, the colloidal state and adsorption compounds in colloidal

platinum, colloidal antimony sulphide, lanthanum blue, molybdenum blue, and colloidal gold solutions. The theories of Werner are illustrated by a large number of metal-ammonia compounds. The book closes with a valuable chapter on methods of preparing the rare elements, including radium, from their ores. These few references will suffice to show the nature and scope of the book which is written from the modern physical-chemical standpoint; indeed, much of the volume might be called physical chemistry, theoretical and applied.

It is scarcely necessary to say that this is not a book for the average undergraduate; students who have some knowledge of chemistry and familiarity with laboratory work will find its study fascinating and stimulating. E. R.

PRACTICAL TESTING OF GAS METERS. By C. H. STONE, B.S., M.S., Chief Inspector of Gas, Public Service Commission, Second District, New York. New York: John Wiley & Sons; London: Chapman & Hall, Ltd. 1909. pp. x + 337, 51 Figures. Price, $3.50.

Under this modest title the author presents a handsome volume of 336 pages in which he gives a thorough and most interesting account of photometry, chemical tests, calorimetry, specific gravity, pressure and testing of meters.

To quote the preface, "so far as the writer knows, no book, written by an American and dealing purely with American method of gas manufacture and testing and thoroughly up-to-date, is available to-day." . . . "The writer's chief aim has been to explain clearly, simply and fully such tests as would be of practical service to the gas manufacturer, chemist or photometrist and to make such comments as might guide him in his choice of apparatus or process." . . . Mr. Stone knows his subject thoroughly; he describes in detail the newest methods and the newest improved forms of apparatus. E. R.